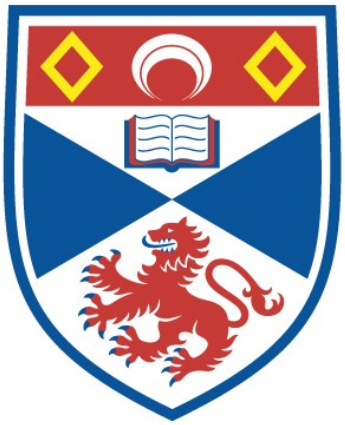
SYNTHESIS OF NOVEL HETEROCYCLIC POLYMERS

John Emans

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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SYNTHESIS OF NOVEL HETEROCYCLIC POLYMERS

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to the

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St. Andrews September 1986

Th A502

This thesis is dedicated to

my parents.

DECLARATION

I, John Emans, hereby certify that this thesis has been composed by myself, that it is a record of my own work, and that it has not been accepted in partial or complete fulfilment of any other degree or professional qualification.

Signed..... Date...9...9...86.....

I was admitted to the Faculty of Science of the University of St. Andrews under Ordinance General No.12 on 1st October, 1983, and as a candidate for the degree of Ph.D. on 1st October, 1983.

Signed..... Date...9...9...86.....

I hereby certify that the candidate has fulfilled the conditions of the Resolution and Regulations appropriate to the Degree of Ph.D.

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CONTENTS

ABSTRACT

This work details the synthesis, characterisation and fabrication of a range of copolyesters, containing various angular disruptors, especially disubstituted 2,5-diphenyl--1,3,4-oxadiazoles.

These disruptors were incorporated into the polymers, to reduce the temperature at which the polymers may be processed, to enable their fabrication into fibres. The majority of the polymers prepared were found to be liquid--crystalline. However, if the angular disruptor content of the polymer was high, it was found that the resultant polymers were non-liquid crystalline.

The polymers were prepared by a melt acidolysis process carried out under a nitrogen flow and subsequently under vacuum, as described in Chapter 3.

Eighteen of the polymers were characterised in some detail, though a measure of the relative molecular weights was thought to be of little importance in this work, since all polymers were of a different composition. Differential scanning calorimetry and hot-stage microscopy revealed that several of the polymers had rather unusual melting behaviour.

The eighteen polymers that were closely characterised were spun into fibres, using a small melt-spinning apparatus that was designed and produced by Bradford University Research Ltd. The resultant fibres were characterised by differential scanning calorimetry, X-ray diffraction and tensile testing.

The general conclusion of the work is that although a reduction in the processing temperature of the polymer is achieved by the incorporation of angular disruptors, which is advantageous, the tensile strength and thermal stability of the fibres produced from such polymers are reduced.

CHAPTER 1

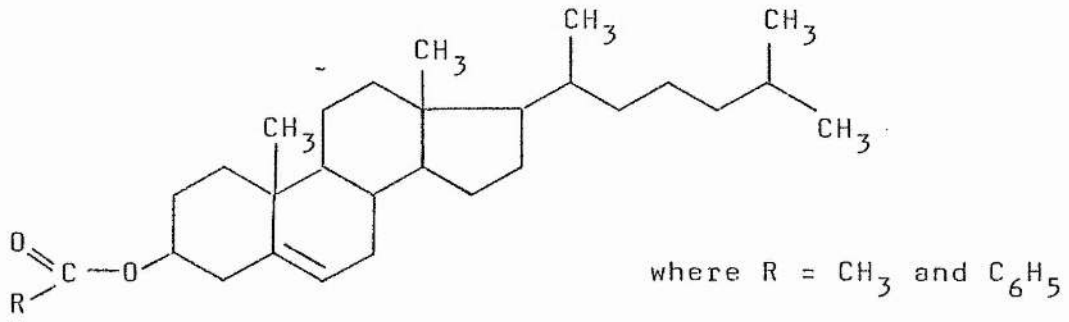
I N T R O D U C T I O N

1.1 LIQUID CRYSTALLINITY

1.1.1 General Introduction

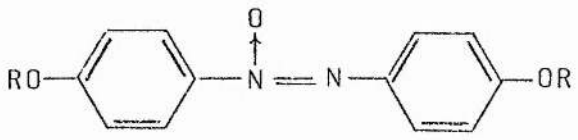
Liquid crystallinity in low molecular weight compounds has been known since 1888, when Reinitzer[1] discovered that cholesteryl acetate and cholesteryl benzoate (Figure 1) possess the peculiar property of melting sharply at a definite temperature to milky liquids; and that the latter, on being further heated, suddenly become clear, also at a definite temperature.

Figure 1



Then in 1890, Gatterman[2] discovered that *p*-azoxyanisole and *p*-azoxyphenetole behaved similarly.

Figure 2



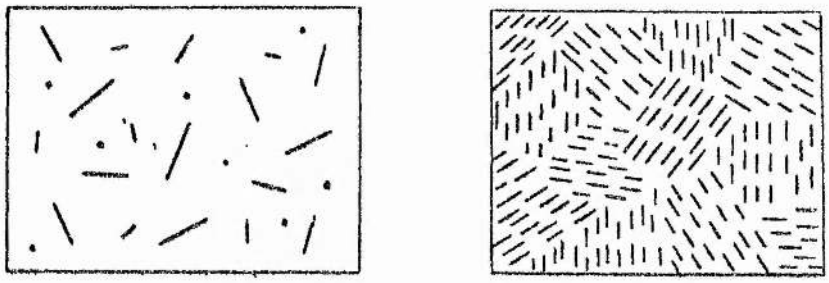
The turbid liquids were found to be endowed with remarkable properties. They flow in the manner of ordinary liquids, but they exhibit double refraction and produce

interference colours in polarised light, which had hitherto been observed only in the case of solid crystalline substances. The turbid liquids were thus anisotropic. To such liquids, in 1904, Lehmann[3,4] gave the name "liquid crystals". However, since the term "crystal" implies the existence of a definite space lattice, which is not found in the case of "liquid crystals", it is better to use the terms "anisotropic liquid" or "mesomorphic state". A systematic classification of the mesomorphic state was proposed by Friedel[5] in 1922, in which the mesomorphic state was subdivided into two main categories, nematic (threadlike) and smectic (soaplike). The cholesteric was considered a sub-class of the nematic.

Once it was believed that the turbid liquids obtained on fusion were heterogeneous, but Lehmann[6,7] was able to prove that these liquids were in fact homogeneous, and that the turbidity of the liquid in bulk was due to a simple optical effect.

The optical and magnetic properties of the anisotropic liquids indicated that certain groups of molecules were orientated in certain directions.[5] The phenomenon may be readily understood on the premises of Bose's "Swarm Theory".[8,9,10] When two or more molecules approach so closely that their centres are separated by a distance less than half the length of the molecules, then free rotation is restricted and the molecules will tend to orient themselves in parallel formations. (Figure 3)

Figure 3



a) Isotropic liquid b) Anisotropic liquid

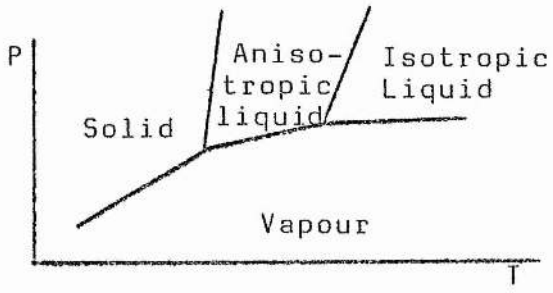
According to Bose swarms of molecules oriented in this fashion will be endowed with a certain symmetry and will thus simulate the behaviour of a uniaxial crystal. Each particular swarm will appear under the microscope as a transparent liquid. The turbid appearance of the liquid in bulk is due to the scattering of the light at the boundaries between the various swarms.

The application of heat will increase the molecular motion and a continuous interchange will occur between the swarms. As the temperature increases, the average size of the swarms diminishes, and the temperature at which the swarms become smaller than the wavelength of light, will be the "clearing temperature". Above this temperature, the liquid is isotropic and singly refracting. In this way, the swarms are quite different from small crystals, since the separate molecules can move freely about certain positions of equilibrium.

It is well established that the transition from the mesomorphous to the amorphous liquid state occurs sharply at

a definite temperature when the pressure is constant, and that the transition temperature varies with pressure. The equilibrium conditions, therefore, may be represented by a diagram, such as Figure 4.

Figure 4



The Swarm Theory is supported by the behaviour of liquid crystals in a magnetic field.[11] It is found that a magnetic field clears droplets of nematic liquid crystals when viewed along the lines of force.[12] When the magnetic force is removed the liquid becomes turbid again. This behaviour may arise from the existence of a permanent magnetic moment, but it is probably more correct to say that it is due to anisotropic polarisation.

So far, the heating of solid crystals to the mesophase is the only type of mesomorphism to be mentioned. With the examples already mentioned, namely cholesteryl acetate, cholesteryl benzoate, *p*-azoxyanisole and *p*-azoxyphenetole, the phase transitions solid crystal → liquid crystal and liquid crystal → isotropic liquid are completely reversible, and this type of mesomorphism is called "enantiotropic". In other cases the mesophase is only observed upon supercooling

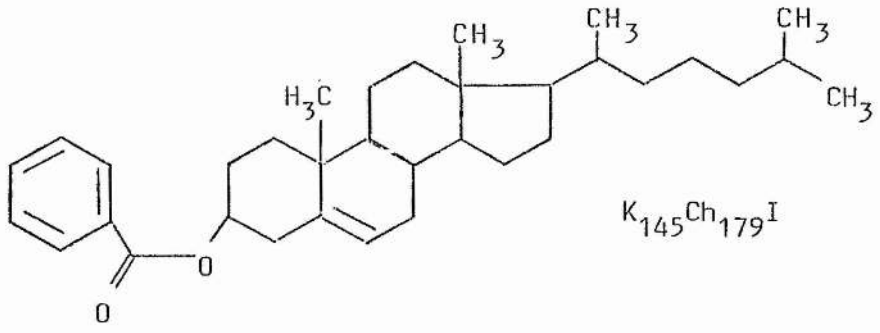
the isotropic melt; this type of mesomorphism is called "monotropic". In the enantiotropic situation, the mesophase is thermodynamically stable, whereas in the monotropic situation, the mesophase is metastable with respect to the solid, and is thus only observed upon cooling. Both the enantiotropic and monotropic mesophases are also called "thermotropic" mesophases since both involve heating the pure solid crystals. Another way in which mesophases can be obtained involves the interaction of solvent molecules and solute molecules. This type of mesophase is called a "lyotropic" mesophase. Both lyotropic and thermotropic mesophases will be explained in greater detail later in the chapter.

1.1.2 Low Molecular Weight Liquid Crystalline Compounds

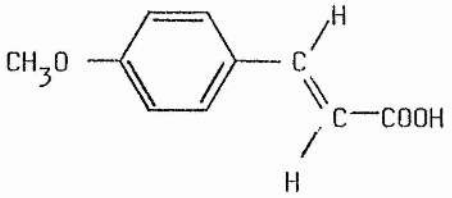
Compounds which form low molecular weight thermotropic liquid crystals have general molecular and physical features.[13] See the examples in Figure 5. They normally possess high axial ratios (*i.e.* length : breadth ratio) (usually in excess of 3); the length being composed of two or more rigid cyclic units, joined directly or by rigid linkages, such as, azoxy, ester and diazo groups. They possess anisotropic molecular polarisations which are an extremely important property of these molecules and is primarily responsible for the various electrooptical effects that have been exploited commercially.

From the last three examples in Figure 5, it is seen that there are several "pathways" from the crystal state to

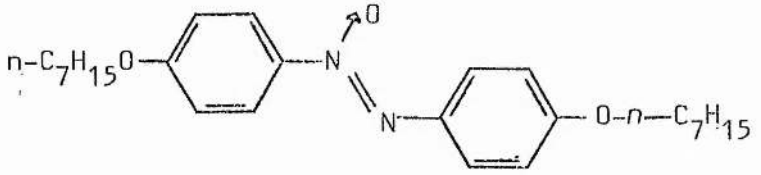
Figure 5



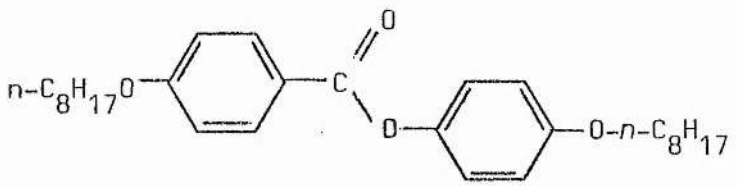
$K_{145}Ch_{179}I$



$K_{170}N_{186}I$



$K_{74}S_{C95}N_{124}I$



$K_{80}S_{C100}S_{A165}I$

Footnote: the temperatures between the symbols represent the transition temperatures between the two phases. The symbols are as follows; K = crystal, N = nematic, Ch = cholesteric, I = isotropic melt and S_A = smectic of type A, *etc.* (See Section 1.1.3.)

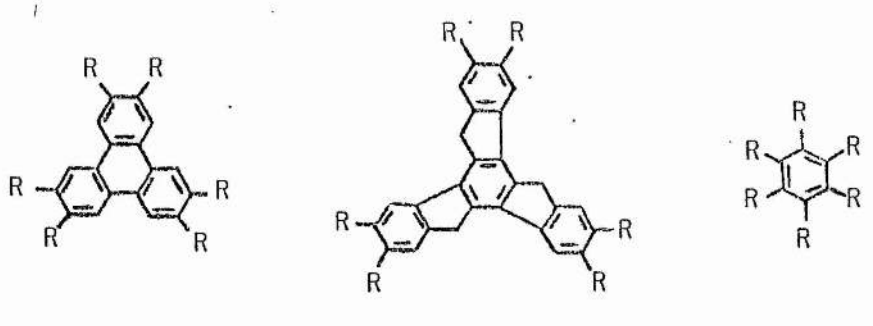
the isotropic melt. Some thermotropic liquid crystals form a nematic phase only, others form a smectic phase only (though in this situation, transitions from one smectic type to another may occur) and others form firstly a smectic and then a nematic.

In general, it is found that the nematic phase is

predominant for compounds with short flexible tails and the smectic phase is predominant for compounds with long tails. Both phases can be seen when the tail is of intermediate length.

Discogens[14] are an entirely different, and more recently discovered type of low molecular weight thermotropic liquid crystalline compound. They are generally composed of a rigid central core, with four to eight flexible side chains. Several of the central cores used to-date to synthesise discogensare shown in Figure 6, along with several side chains.

Figure 6



where R = $n(C_xH_{2x+1}COO)-$, $C_xH_{2x+1}O-$, $n-C_xH_{2x+1}-$

1.1.3 Classification of Mesophases

Nematic, smectic, cholesteric and discoidal liquid crystals differ with respect to the manner and degree of ordering of the molecules.

In nematic liquid crystals[15] the molecules are oriented

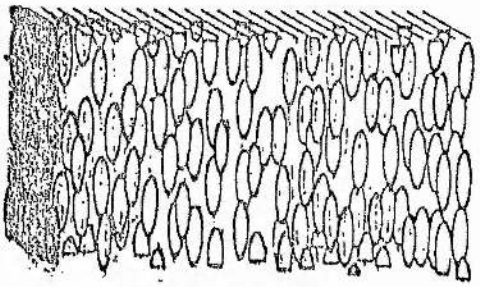
so as to be approximately parallel in local domains. These anisotropic domains are randomly oriented and give the mass the form of a turbid liquid. (See Figure 7)

Cholesteric liquid crystals[15] are a modification of the nematic state in which the molecules are again oriented approximately parallel but in monomolecular layers. The mean direction of the molecules in each successive layer is at a certain angle with respect to the preceding layer; so the layers form a helix. (Figure 7)

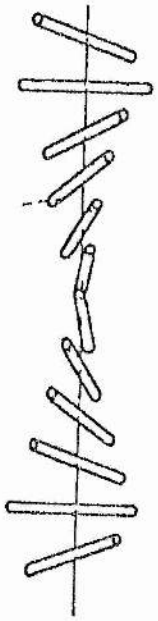
Smectic liquid crystals,[15] of which there are eight varieties, are composed of layers, which are parallel and freely sliding with respect to one another. The layers have a depth of only one or two molecules, which are oriented orthogonally to the plane of the layer or in two cases, inclined towards it. Within the layers the molecules can be arranged in several ways. Smectics A and C can best be described as a layered nematic configuration, where the molecules can move freely in two dimensions, relative to one another. With increased order within the layers, the other smectic types arise. With hexagonal lattice-type packing, smectics B and H are obtained. A cubic lattice type structure results in smectic D. Smectics F, G and E arise from nearly perfect packing of the molecules. Smectics C and H are formed by chiral molecules and it is these two structures which contain the molecules that are inclined to the layer plane. (Figure 7)

Discoidal liquid crystals,[15] like smectics, have a variety of structures. There are however two very different

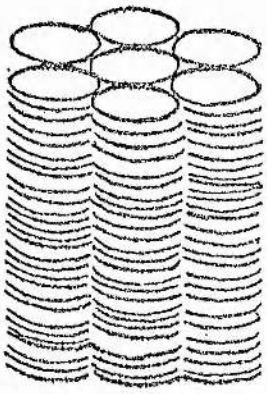
Figure 7



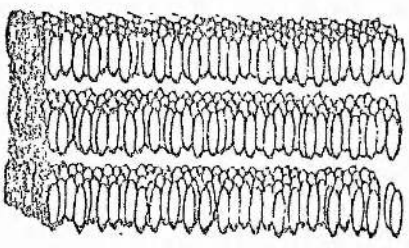
Nematic structure



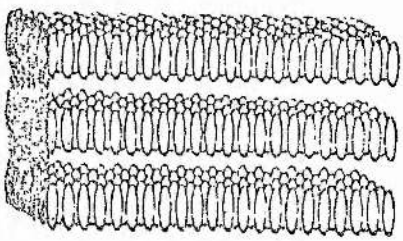
Mean molecular direction in cholesteric phase



columnar discoidal phase



Smectic A



Smectic B

classifications in structure; columnar and fluid. The first structure consists of stacks or columns of molecules, which can be arranged hexagonally or rectangularly. The columns can be tilted and have regular or irregular packing. In the second structure, the centres of the molecules are randomly distributed, but the planes of the molecules are, on average, parallel. (Figure 7).

1.2 HIGH PERFORMANCE MATERIALS

1.2.1 General Introduction

Recent demands for high performance materials for industrial, engineering and military requirements have led to a phenomenal growth in research in this field. It is increasingly evident that conventional organic polymers, such as poly(ethylene terephthalate), polyethylene and polystyrene, and inorganic materials such as glass, asbestos and steel, are deficient in certain desired properties.

As a whole, these modern materials should possess high strength and modulus, high thermal stability, and low creep, thus resembling the traditional engineering fibres such as glass, graphite and steel. They should also possess the best features of organic fibres, such as low density, easy processability, good fatigue and abrasion resistance. Additional desirable properties are high melting point, low smoke and toxic gas emission, and inertness to chemicals and radiation, even after long periods of exposure.

The high mechanical properties of these inorganic materials are due to their structures. The three-dimensional

structures, as in that of steel, can effectively spread any load or strain that is applied through the lattice, so reducing local strains that may result in fracture. The fact that the theoretical modulus of a polymer should approach that of steel (see Table 1), has been known for many years.[16,17] However, conventional polymers, such as poly(ethylene terephthalate) and polyethylene, were found to have moduli significantly less than those predicted. Polyethylene and polypropylene, for example, are composed of alkyl chains, which are flexible and so form entangled, twisted arrangements. This randomness in structure reduces the proportion of tie molecules - molecules which link one region of crystallinity to another such region - and subsequently imparts a low load-bearing capacity to such polymers.

In order to increase the load-bearing strength of a polymer, it is necessary to increase the proportion of tie molecules. This is best envisaged in a highly oriented and extended structure, wherein a higher proportion of the polymer chains are fully extended and aligned. If one hundred percent extension and alignment were possible, then the continuous crystalline structure producing the theoretical modulus would be achieved.

To increase the degree of extension and alignment, two approaches were developed. The first was a way of physically altering the morphology of conventional polymers to produce these materials with improved mechanical properties. The other approach was more fundamental in nature and involved

altering the chemical structure of the polymer chain itself. The alkyl chains of polyethylene and polypropylene were replaced by the more rigid 1,4-phenylene unit, linked by ester, amide, azo and other rigid groups to produce chains, which reduced or removed the degree of bending, giving greater extension and alignment.

TABLE 1

Theoretical Modulus Values for Some Polymers and Other Materials[18]

Material	Modulus (GPa)
Polyethylene	240
Polypropylene	42
Polystyrene	12
Polyoxymethylene	53
Poly(vinyl alcohol)	250
Poly(ethylene terephthalate)	137
Carbon steel	208
Aluminium	69
Glass Fibre	69 - 183

1.2.2 Physical Approaches

Several techniques have been employed to produce conventional polymers of high mechanical properties, *e.g.* superdrawing, drawing from dilute solutions, gel spinning and the extrusion of supercooled melts. Polyethylene was the polymer most often used since its simple composition allows the determination of morphological transformations and because it presents one of the highest theoretical moduli.

The earliest attempts to produce high-modulus fibres

from polyethylene involved the tensile drawing of the polymer at elevated temperatures. Polyethylene fibres with a modulus of 35 GPa were obtained by Takayanagi[19] by drawing melt-extruded fibres of the polymer. Peterlin[20] produced polyethylene fibres with modulus 27 GPa at a draw ratio of 20, and Fischer[21], using a draw ratio greater than 15, increased the modulus to 38 GPa. However, some of the best fibres produced were prepared by Capaccio[22], who, with a draw ratio of 30, obtained a modulus of 70 GPa.

A two-step process was developed by Clark and Scott[23] for polyethylene, polypropylene and polyoxymethylene. A modulus of approximately 70 GPa was again obtained for polyethylene. The first step involved drawing the polymers to their natural draw ratios quickly, and the second step involved the slow superdrawing of the polymers at selected temperatures.

Ultra-high modulus polyethylene was prepared by a technique of controlled precipitation, developed by Pennings[24] with modulus up to 100 GPa; that is approximately 40% of the theoretical value, which indicates a large percentage of fully extended chains. The process involved the longitudinal growth of fibrillar polyethylene crystals, with molecular weights of up to 1.5×10^6, from a xylene solution of temperatures above 100 °C, with growth rates of up to 150 cm/min. The growth process is affected by many factors; the take-up speed, rotor surface and speed, polymer concentration and crystallisation temperature.

Extrusion techniques have been widely used for the processing of polymers since as early as 1968, giving oriented extrudates by passing the melt through a capillary rheometer with a conical die. Both direct ram and hydrostatic techniques have been found to give equally good results, if conditions are carefully selected. Southern and Porter[25] obtained transparent and fibrous polyethylene extrudates by pushing the melt (132 - 136 °C) above a critical shear rate through a capillary rheometer and conical die. The resulting higher extrusion pressure combined with the high elongational velocity gradient caused the polymer to supercool, which led to a massive crystallisation within the conical die. Subsequent modifications of the process followed, *e.g.* using a conical die with a tapered die angle not greater than 8°[26], increasing the extrusion draw ratio, and varying the temperature.

The spinning of a dilute solution of polyethylene to obtain an extrudate of untangled polymer chains, has been achieved by gelling the spun solution in a cold zone.[27,28] The gelled fibre precursors have then been subjected to hot drawing, either directly or after removal of the solvent at ambient temperature. Filaments of polyethylene with moduli of 90 GPa have been prepared by this method.

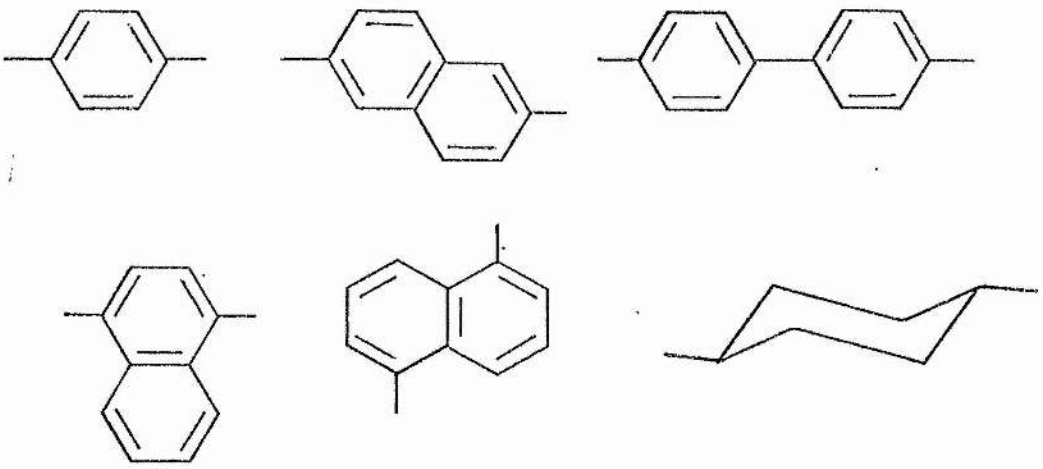
1.2.3 Chemical Approaches

Linearly rigid polymers can be sub-divided into two categories. The first (and smaller) class consists of a helix, where each successive turn is held in place through

steric hindrance or intramolecular forces. The bonds contained in the polymer chain may be flexible as in the α-helical form of polypeptides.

The majority of rigid chain polymers, however, fall into the second category. These polymers consist of a succession of rigid units with chain-continuing bonds which are collinear or parallel and oppositely directing. See Figure 8.

Figure 8

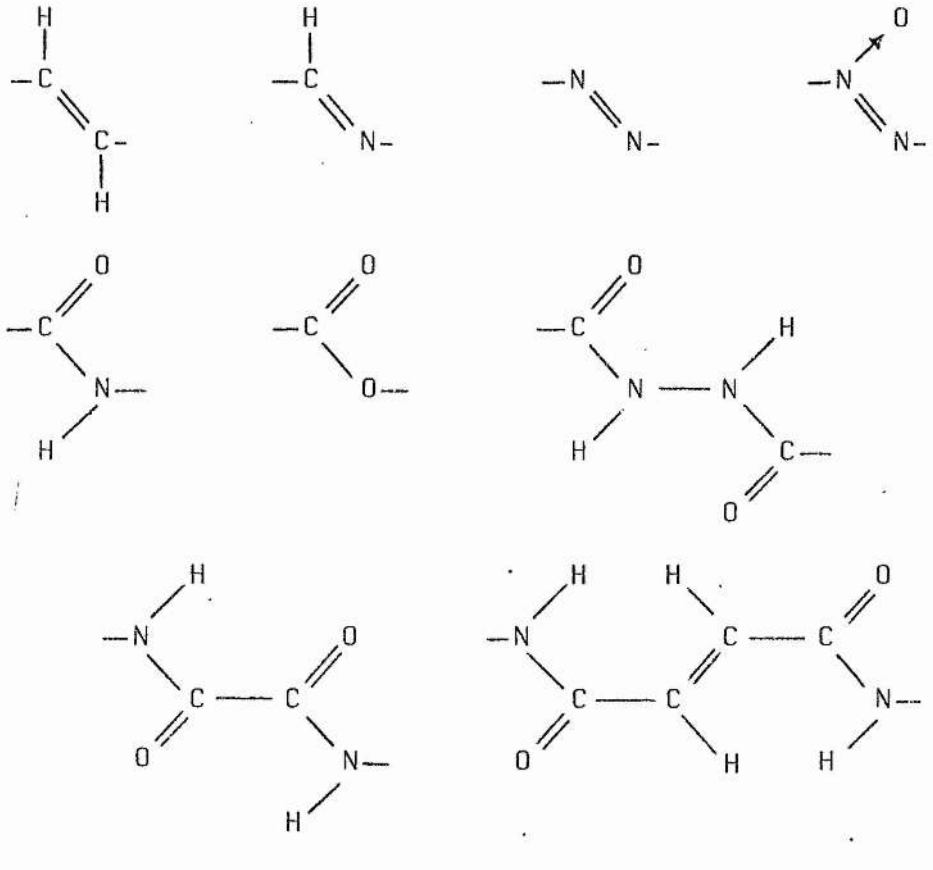


The ring structures are inherently rigid and are the main orientation-maintaining components in the chain. The ring need not necessarily be aromatic in nature, as evidenced by *trans*-1,4-cyclohexylene.

The ring structures may be connected directly, by a single covalent bond, or by non-cyclic units. The latter, once again, have the common feature of having chain-continuing bonds which are collinear or parallel and oppositely directing. Examples are given in Figure 9. The *trans* geometry necessary for such an arrangement is

maintained through double bonds or by a significant energetic preference for that conformation, as in the case of the ester and amide groups.

Figure 9



It is evident that these structural units are very similar to those found in low molecular weight liquid crystalline compounds. It is not therefore unreasonable to predict that these polymers may be capable of forming mesophases, either in solution (lyotropic), or in the pure state at elevated temperatures (thermotropic).

1.2.4 Theoretical Basis for Liquid Crystallinity in Rigid-Chain Polymers

Lattice theories[29-37] have proved to be very successful in predicting the criteria for the occurrence of liquid crystallinity in polymers. In 1956, Flory[29] first performed theoretical calculations on rigid and semi-rigid polymers to formulate the criteria for the formation of a single anisotropic phase in solution. He regarded the polymer molecules as being composed of rigid segments. The polymer molecules did not interact with neighbouring molecules; the only interaction considered was the repulsion which arises due to the overlap in space of two molecules.

The possibility of obtaining thermotropic polymers was considered theoretically, first by Papkov *et al*[38], and then by Ciferri.[39] However, the possibility of obtaining such polymers was implicit in Flory's treatment of the rigid-rod situation. The criteria postulated in Flory's theory can also be interpreted as applying to polymers where the solvent concentration is zero, and therefore to thermotropic as well as lyotropic systems.

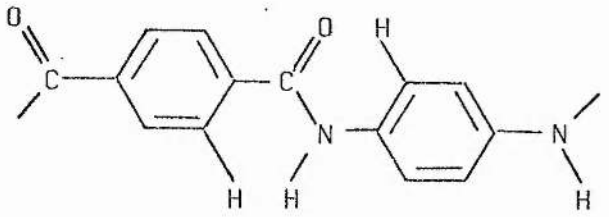
Thus theory predicts that rigid-rod polymers can form mesophases and experimental observations confirm these predictions. The helical chain class of polymers will not be further mentioned, since they lie outwith the scope of this project. The class of polymer consisting of rigid-ring backbones, will only be discussed. The two main categories to fall within this class of polymer are polyamides and polyesters.

1.3 POLYAMIDES

1.3.1 The Conformation of the Polyamide Chain

The conformation of aromatic amide polymers is governed by inter- and intra-molecular forces. There is no appreciable double-bond character in the carbonyl C-N bond (MNDO calculations give a bond order of 1.13[40]), and so π-overlap with the aromatic rings can be effectively discounted. (Figure 10).

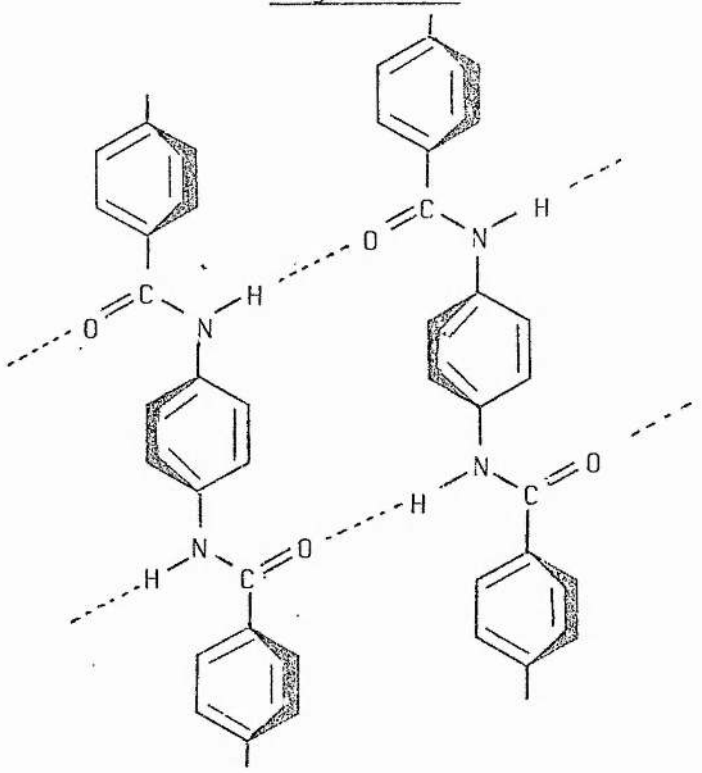
Figure 10



Steric interaction between the oxygen and the *ortho*-hydrogen of the *para*-phenylene diamine segment, and between the amide hydrogen and an *ortho*-hydrogen of the terephthaloyl segment occurs, and due to these intramolecular interactions the interplanar angle between the phenylene and the amide segments range from 25 - 40 °.[41] (Figure 11)

If the polymer has a regular structure as has poly(*p*-phenylene terephthalamide), then the amide links are regularly positioned, and this allows the formation of medium-strong intermolecular hydrogen bonding. This long-range cohesive force between the chains, leads to these polymers having exceedingly high melting points, to the extent that prior degradation may occur. This makes the

Figure 11



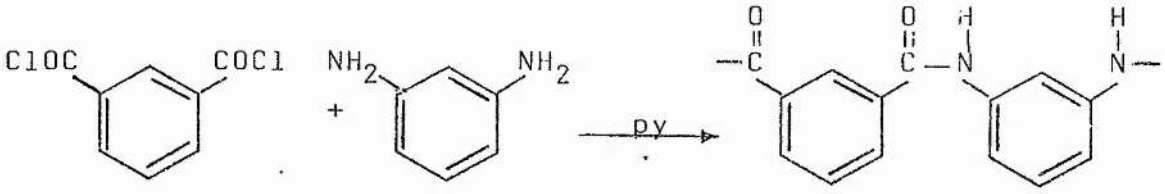
manufacture and processing of these materials impossible in the solid state, and thus polyamides are generally synthesised and processed in solution.

1.3.2 The Synthesis of Polyamides

The most important industrial process used to prepare polyamides is the low temperature reaction of bis acid chlorides and diamines.[42] (Scheme 1) This route is the simplest and most direct route to the preparation of polyamides of high molecular weight. The polymerisation is carried out in an amide solvent (to which lithium salts may be added, to increase the polymer solubility) or in a polychlorohydrocarbon with amines, to form hydrochloride salts.[43] The reaction temperature and choice of solvent are particularly important factors in preventing premature

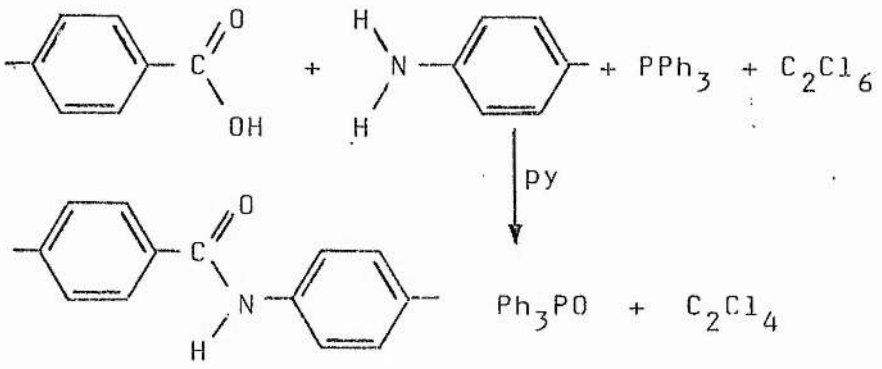
precipitation, which would form polyamide of low molecular weight.

Scheme 1



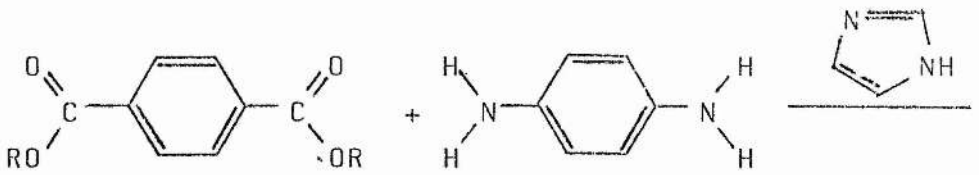
Other methods that have been used for polyamide synthesis include the amidation-style reaction of aromatic acids and amines with a phosphorus(III) compound in amine or amide solvents, using organic halogen compounds as co--reactants.[44] (Scheme 2) Lithium salts may again need to be added to increase the polymer solubility to prevent premature precipitation.[45]

Scheme 2

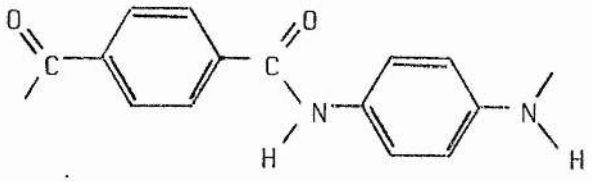


The imidazole-catalysed reaction of aromatic acids, or their esters, and amines has also been used to prepare polyamides.[46] (Scheme 3) Derivatives of imidazole can also be used as the catalytic agent.

Scheme 3

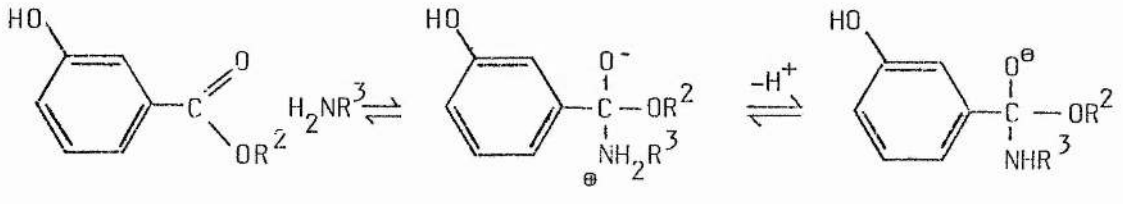


R = H or alkyl

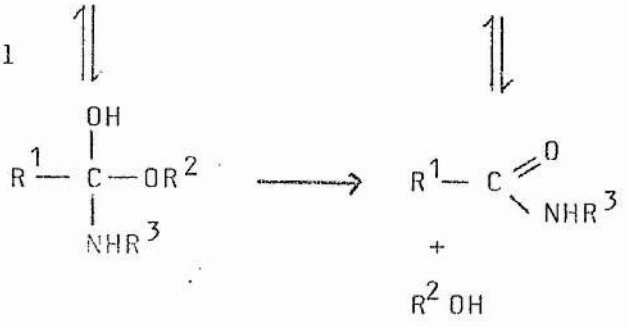


Although the aminolysis of esters is less frequently used, than say the acylation of amines with acyl halides or anhydrides, to produce amides, active esters, such as those of substituted phenols have been used to prepare aromatic polyamides using unhindered amines under mild conditions with reasonably high molecular weight. (Scheme 4)

Scheme 4



where R^1 = substitued phenol



1.3.3 The Historical Development of Polyamides

The first wholly aromatic polyamide developed and commercialised was "Nomex", based upon poly(m-phenylene isophthalamide) (Figure 12). Nomex has high resistance to combustion, is non-melting and has a high durability up to temperatures of 250 °C, but degrades rapidly at approximately 370 °C. It has excellent resistance to chemicals, but very poor resistance to light, and is thus commonly coated.

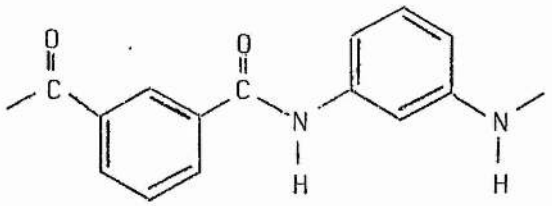
For the manufacture of fibres from the polymer, two methods were developed. In the first method,[47] the polymer was prepared by the reaction of isophthaloyl chloride and m-phenylenediamine in methylene chloride and triethylamine. The precipitated polymer was dissolved in a solution of lithium chloride in dimethylformamide (5/95, w/w) and dry spun at 128 °C, into a chamber at 225 °C, washed and finally drawn at a draw ratio of 4.75. The second method was more direct. The polymer was prepared in dimethylacetamide, from which it did not precipitate. The solution was neutralised and then dry spun to produce fibres.

Nomex has many uses, *e.g.* protective clothing, for fabrics in critical areas such as aircraft; but its largest use is in making paper for high temperature electrical insulation and structural laminates.

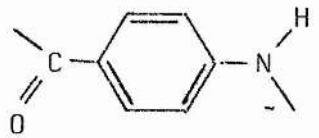
There was a considerable improvement in the thermal stability of Nomex compared to conventional polymers.[41] However, although the problem of chain flexibility was substantially reduced, due to the *meta* configuration of the

rings, the degree of orientation was low as the chain continuing bonds were not collinear or parallel and oppositely directing. As a result, solutions of Nomex are isotropic.

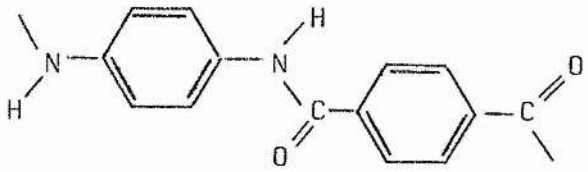
Figure 12



Nomex poly(*m*-phenylene isophthalamide)



Fibre B polybenzamide



Kevlar poly(*p*-phenylene terephthalamide)

All-*para* analogues were then developed. The first of these was "Fibre B",[48] based upon polybenzamide, but this was subsequently replaced by "Kevlar" which was based upon poly(*p*-phenylene terephthalamide).[49]

These all-*para* polyamides can under certain conditions form liquid crystalline solutions. The criteria for the formation of a nematic phase, instead of an isotropic phase, are

a) the polymer concentration must be above a critical value;

b) the molecular weight of the polymer must be above a critical, high value;

c) the temperature must be below a critical value.

Such critical values vary from solvent to solvent There are also critical values of solvent composition. These critical values are interdependent and not absolute.

One of the most important features of these lyotropic solutions, is the alignment of the local nematic domains at low shear rates. This results in the apparent viscosity in the anisotropic phase being low compared to that of the isotropic phase obtained at higher temperatures. Under extensional flow, such as encountered in fibre formation, the degree of parallel alignment of the nematic domains is very large and produces fibres similar to or greater in tenacity than conventional fibres which have been drawn.

Fibres are normally obtained from such lyotropic systems by a process known as dry-jet-wet-spinning, where the polymer solution is passed through a spinnerette into a coagulant at low temperature, which effectively immobilises the individual polymer chains within the fibre, so increasing the alignment of molecular chains and leading to the formation of high tenacity materials. Such fibres have mechanical properties that greatly surpass those of conventional undrawn fibres and even the majority of drawn fibres. Further improvements can be made by annealing these products at high temperature.

The best example of such high tenacity, high initial modulus fibres is Kevlar.[43] The polymer is prepared by the

low temperature reaction of terephthaloyl chloride and *p*-phenylene diamine in hexamethylphosphoramide or N-methyl-pyrrolidone. The precipitated polymer is collected and washed, and dry-jet-wet-spun as a 20% solution in concentrated sulphuric acid, at a temperature of 80 °C, into a coagulant at approximately 5 °C. The fibres thus collected are termed Kevlar 29 (Table 2). Tensioned fibre treatment of Kevlar 29 at approximately 500 °C for 3 seconds, produces Kevlar 49; a more highly oriented crystalline structure, with improved mechanical properties (Table 2).

Mechanical properties apart, Kevlar has properties very like that of Nomex. The uses of Kevlar are varied; it is used in protective clothing, bullet-proof vests and military helmets; as a reinforcing material for plastics and rubbers; aerospace and aircraft composites; sports equipment; transmission belts, tyres and high pressure hoses and ropes.

Although Kevlar has found great use in many fields, it can only be fabricated into fibres and films. This is a major deficiency, which has to be overcome if shaped articles are required.

Table 2

Physical Properties of High-Strength, High-Modulus and Other Fibres

Fibre	Youngs Modulus (GPa)	Tensile Strength (GPa)	Extension (%)	S.G. g/cm^3
PET*	12.0	1.0	10.5	1.38
Nylon 6,6*	5.0	0.9	13.5	1.14
Nomex	17.3	0.7	22.0	1.40
Kevlar 29	59.0	2.7	4.0	1.44
Kevlar 49	127.0	2.9	2.6	1.45

*high tenacity

1.4 POLYESTERS

1.4.1 The Historical Development of Polyesters

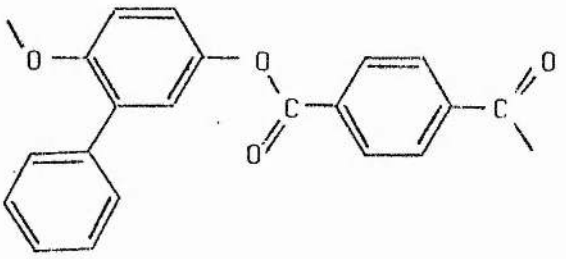
I.C.I.[50,51] and the Carborundum Company,[52] were both involved in the sixties with the preparation of aromatic polyesters. However, the liquid crystalline nature of these polymers went unnoticed, and it was not until 1975 that it was noted in the literature that some aromatic polyesters composed of a main-chain comprising rigid-rod and flexible segments, had thermotropic character. In the same year, Roviello and Sirigu[53] described a polyester composed of alternating rigid-rod and flexible segments, the rigid segments being derived from a low molecular weight thermotropic liquid crystal. In 1975, the Du Pont Company[54] describes a range of highly aromatic polyesters with a substantial degree of extended-chain conformation, and Jackson and Kuhfuss[55] of the Tennessee Eastman Company, describe the random copolyesters of poly(ethylene terephthalate) with poly(*p*-oxybenzoyl). Since these initial papers, much investigation into aromatic polyesters has taken place.

Thermotropic melts are in many ways similar to the lyotropic solutions used to produce fibres. Their observed viscosity is very much lower than an equivalent isotropic melt of similar molecular weight. The orientation of the liquid crystalline melt is achieved by the shear applied at the spinnerette. A high degree of orientation is thus obtained in the "as spun" fibres, even at low take-up speeds.

These fibres have mechanical properties akin to those prepared from lyotropic solutions: low extensibility; high

modulus and high tenacity. These properties are quite remarkable when the molecular weight of the polymer is considered. The "as spun" fibres, made by Jackson,[56] from poly(phenyl-p-phenylene terephthalate) (Figure 13) had a tensile strength of 0.77 GPa, (assuming a density of 1.45), where the mean molecular weight was approximately 5,000 (*i.e.* 16 repeat units). An equivalent tensile strength for

Figure 13



poly(ethylene terephthalate) would require a molecular weight of 30,000. The tensile properties of the "as spun" fibres can be improved, as with those from lyotropic systems, by heat treatment.

Thermotropic polymers are potentially of more importance than lyotropic polymers. Thermotropic systems fit in well with conventional melt processing techniques and shaped articles can be readily prepared. Thus the limitation of fibres and films only, is overcome.

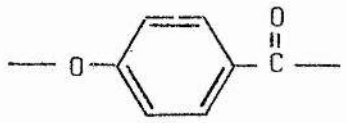
Many of the original copolyesters prepared were of too high a melting point to permit the spinning of fibres, without reduced mechanical properties, due to degradation at such temperatures. Attempts were thus made to prepare polyesters of lower melting point, suitable for processing.

1.4.2 The Development of Melt Processibility in Polyesters

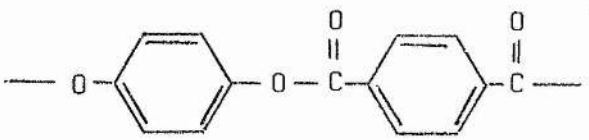
The high melting points of homopolyesters are a result of the high degree of crystallinity of such symmetrical molecules. Even without the inter-chain forces found in amides, considerable disruption of main-chain order is necessary to depress the crystallinity, and thus lower the melting point.

The homopolyesters (poly(*p*-oxybenzoyl), poly(*p*-phenylene terephthalate) and poly(*p*-phenylene naphthalene-2,6-dicarboxylate), (see Figure 14), are reported to melt at 610 °C,[56] 596 °C and 577 °C[57] respectively. These temperatures are too high to permit the formation of a stable nematic phase. Also at these temperatures, degradation can be expected to be extensive and thus such melting points cannot be looked upon as a standard phase change.

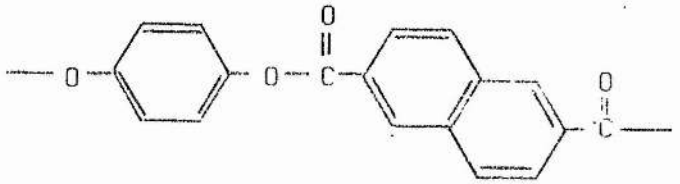
Figure 14



poly(*p*-oxybenzoyl) 610 °C



poly(*p*-phenylene terephthalate) 596 °C



poly(*p*-phenylene naphthalene-2,6-dicarboxylate) 577 °C

To impart melt processibility, some disorder is introduced in the polymer chain. These disordered chains are less regular in structure, preventing efficient packing of the molecules. The quality of crystallinity is thus reduced and this in turn leads to a depression in the melting point. Increased disorder can also be achieved by random copolymerisation, *e.g.* the homopolymer (poly(*p*-oxybenzoyl) melts at 610 °C and the homopolymer poly(*p*-phenylene terephthalate) melts at 596 °C, but a 50:50 random copolyester from these two monomers melts at 510 °C.[56] Unfortunately this melting point is still too high for easy processibility: a further depression of around 200 °C is required. In the above example, all the structural units are similar, and randomisation is in the direction of the ester linkages. A substantial decrease in crystallinity, and hence in the melting temperature, is obtainable if the *p*-phenylene segments are randomly replaced or altered. This is best done by incorporating one or more of the following structural units:

a) aromatic nuclei with additional substituents,

b) polycyclic aromatic systems,

c) angular elements,

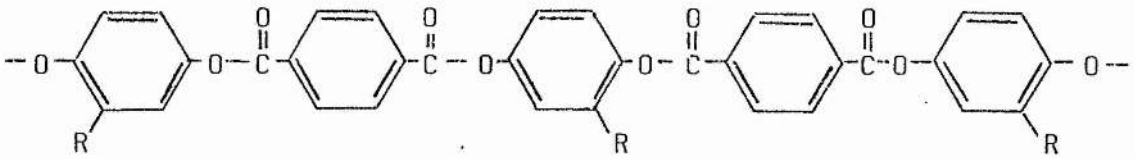
d) aliphatic spacers.

Substituted Aromatic Nucleus

In rigid-rod polymers composed of alternating *p*-phenylenedioxy and *p*-terephthaloyl rings, *i.e.* a polymer of type AA-BB, the *p*-disubstituted rings have a plane of symmetry normal to the chain axis. A single substituent in

either ring brings about copolymerisation and destroys the plane of symmetry, as a result of random head-to-head and head-to-tail configurations. The crystal lattice is thus disrupted and in some instances the crystallinity can be completely eliminated. (Figure 15)

Figure 15



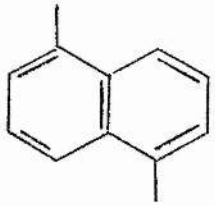
Several patents[50,51,58] demonstrate the technique well. It was found[58] that a substituent in the *p*-phenylenedioxy ring has a greater effect than the same substituent in the terephthaloyl segment.

The size of the substituent is important. Methyl- and chloro-substituted rings are particularly effective in lowering the melting point. Fluoro- was found to be too small, whereas larger substituents, such as methoxy and bromo reduce the stability of the nematic phase. However, even substituents as large as phenyl and p-tolyl have been found to be effective in producing nematic melts.

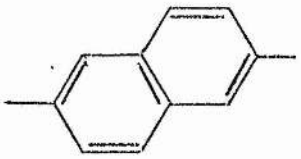
Polycyclic Aromatic Systems

The most commonly used species in this class of disrupter, are those based on naphthalene. The two isomers used are the 2,6-naphthylene and the 1,5-naphthylene units, since both are mesogenic although the incoming and outgoing bonds are not collinear. (Figure 16)

Figure 16



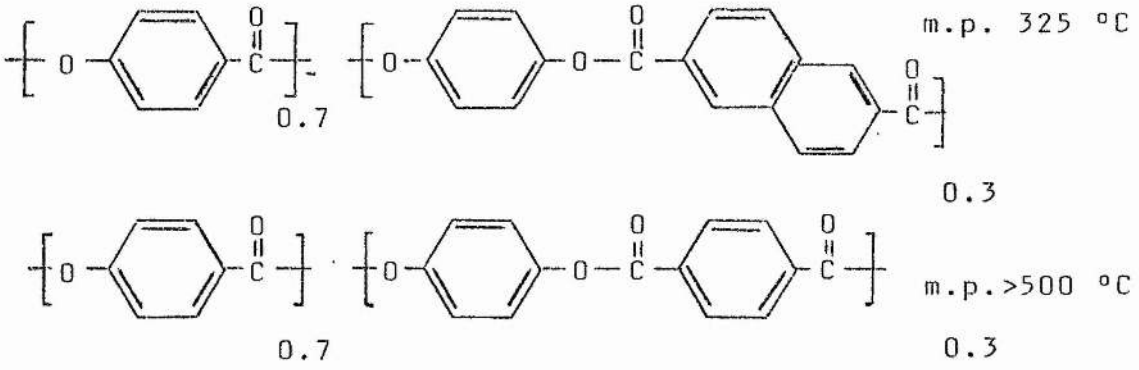
1,5-naphthylene



2,6-naphthylene

The 2,6-naphthylene unit appears to be the most effective as a melting point depressor. For example see Figure 17.

Figure 17



In polymers containing 2,6-naphthylene segments, a small amount, (up to 20%), of amide linkages may be present without any effect on the thermotropic properties of the polymers.[59]

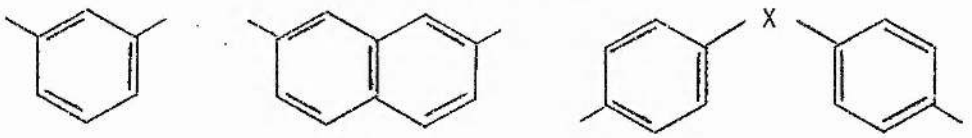
The above examples of producing melt-processible polymers are of particular interest because they contain only mesogenic units, and highly oriented samples are expected to have higher moduli than those derived from copolymers which contain angular or flexible segments.

Angular segments

Any structure with an angle other than 180° between linking bonds is going to introduce a bend into the polymer chain. For examples see Figure 18.

Although such angular segments are very effective at reducing the melting point of polymers, their usage is kept

Figure 18



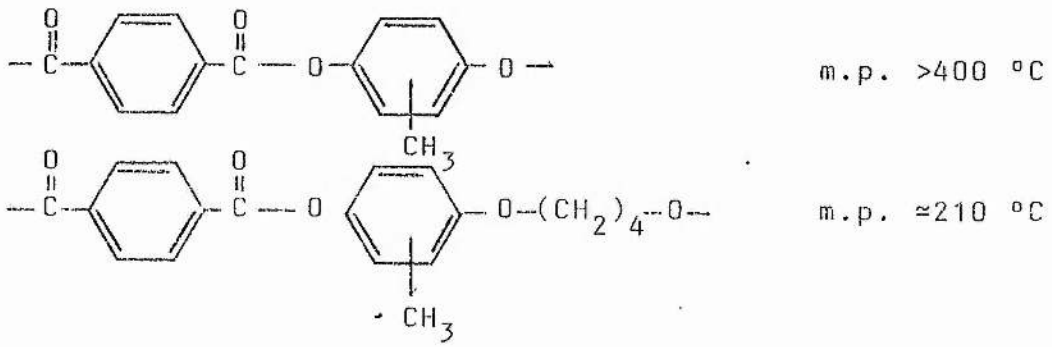
Where X = O,  *etc.*

to a minimum or avoided altogether because they are firstly non-mesogenic[60] and consequently they tend to have an adverse effect on the mechanical properties of the resultant polymers.[61]

Aliphatic Spacers

The incorporation of aliphatic spacers is a departure from the rigid-rod nature of segments used in the three previous methods. The flexible, aliphatic spacers do however create a large depression in melting temperature.[61] For example see Figure 19.

Figure 19



The incorporation of non-mesogenic units, either angular or aliphatic may suppress the formation of a mesophase altogether, if the proportion of non-mesogenic units exceeds a critical limit.

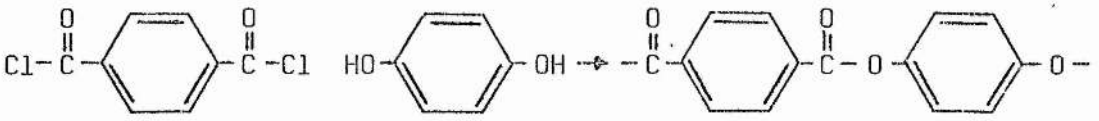
For the formation of a mesophase, there are two requirements to be fulfilled. Firstly, the rigid-rod unit must have a certain length and length:diameter ratio and secondly, the flexible spacer must not exceed a certain length. These lengths depend on the rigid-rod structure, and the flexible spacer's structure. The nematic phase stability is increased with increasing length and length: diameter ratio of the rigid-rod unit, and with decreasing length of the flexible spacer.

1.4.3. The Synthesis of Polyesters

One of the most limiting factors in the preparation of polyesters, is their very low solubility in most commonly used solvents. There are four basic reactions used to produce polyesters several of which are very similar to those used to prepare polyamides. (See section 1.3.2)

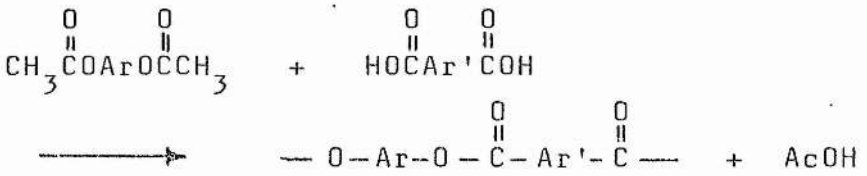
The first method is the Schotten-Baumann reaction of an acid chloride and an alcohol, and is carried out in two different ways. The first way involves the reaction of the monomers in solution at high temperature, usually in a polychlorohydrocarbon with tertiary amines. The second is a melt reaction of the two monomers; the hydrogen chloride by-product is removed in an inert gas flow or by vacuum.[62] (Scheme 5).

Scheme 5



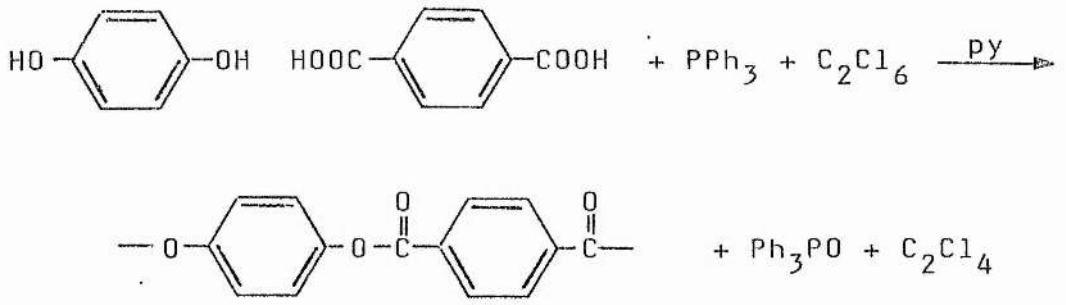
The second method is a trans-esterification, performed in the melt at high temperature. Again there are two variations of this reaction. The first uses the diphenyl esters of aromatic dicarboxylic acids and difunctional phenols, whereby phenol is produced as by-product.[63] The second variation uses the diacetates of difunctional phenols and dicarboxylic acids and acetic acid is the by-product produced.[64] Both by-products are removed by vacuum. The latter variation was used to form the copolyesters in this work. (Scheme 6).

Scheme 6



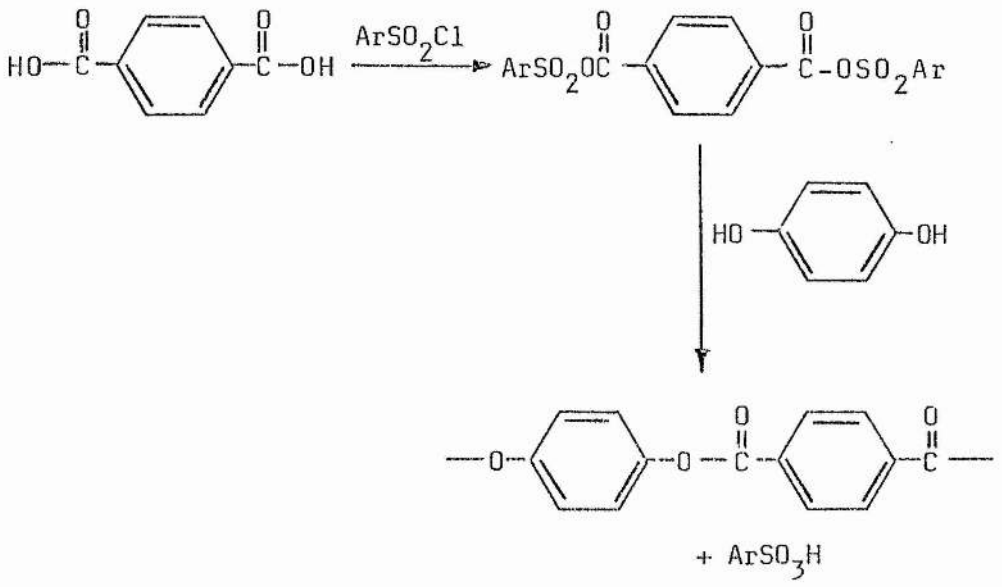
The third method involves the reaction of an aromatic acid with a phenol, in the presence of a phosphorus(III) compound with a polychlorohydrocarbon solvent as co-reagent with lithium chloride, added for solubility reasons, in pyridine or other amide solvents.[65] (Scheme 7).

Scheme 7



The last method of polymerisation involves the formation of mixed anhydrides *"in situ"*. The use of arylsulphonyl chlorides, for example, is used to effect the direct reaction of aromatic dicarboxylic acids with difunctional phenols, and is believed to proceed *via* the production of a mixed sulphonic-carboxylic anhydride.[66] (Scheme 8).

Scheme 8



All the above reactions can be applied to the formation of copolyesters as well as to polyesters.

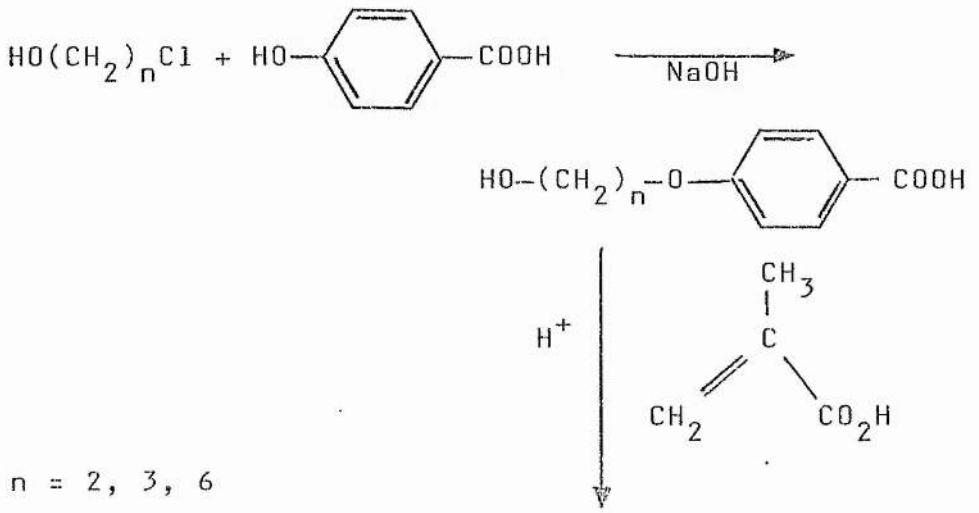
1.4.5 Side-Chain Liquid Crystalline Polyesters[67]

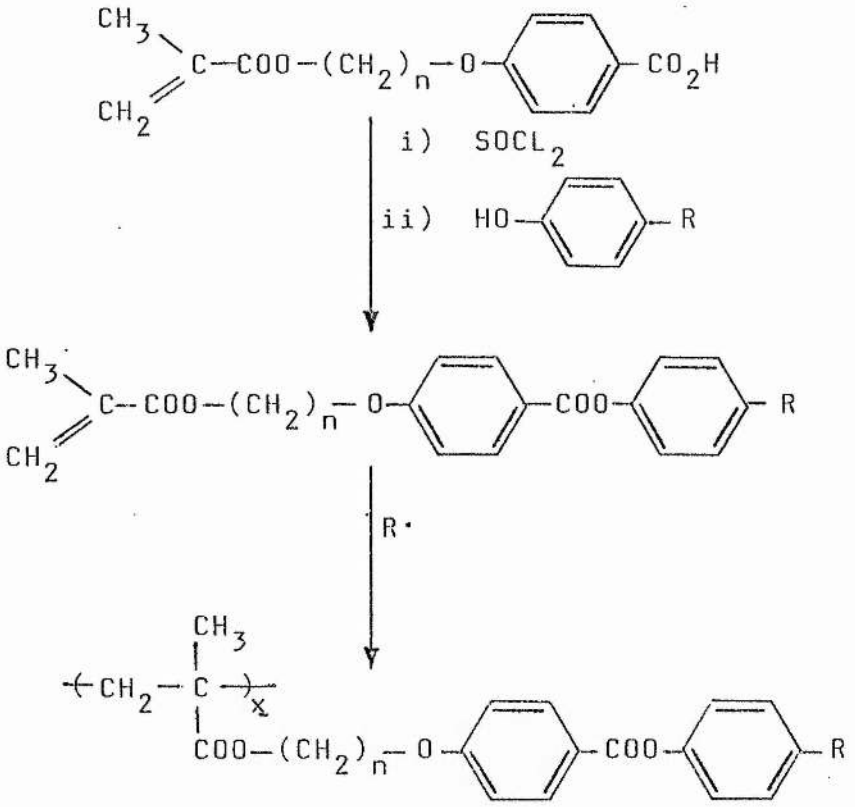
In these polyesters the mesogenic unit is connected by a flexible spacer group, usually composed of methylene units, to a flexible polymer chain, generally based on vinyl, methylvinyl or siloxane. The flexible connection allows for the interactions of the pendant mesogenic unit to be detached from the main-chain motion.

These polymers are most commonly prepared by radical--initiated reactions, giving atactic polymers of high molecular weight. These polymers, like main-chain polymers can form smectic, nematic and cholesteric phases.

There are two routes applied to the synthesis of these polymers. The first is the vinyl polymerisation of the pendant units: the second involves the addition of the pendant units to a preformed polymer.[68] The first route is the more commonly employed; an example is shown in Scheme 9.

Scheme 9





1.5 THE POLYMERIC MESOPHASE

1.5.1 General Features

It has been assumed so far, that polyamides form only lyotropic systems, and polyesters, albeit some may possess a proportion of amide linkages, form thermotropic systems. This linkage to specific liquid crystalline system correlation is however, not to be taken strictly. For although the majority of lyotropic systems are amide-based, and thermotropic systems ester-based, there are undoubtedly aromatic polyesters which show liquid crystallinity in solution, and a thermotropic polyurethane has recently been reported.[69]

With respect to polymeric mesophases, it was suggested that the term "ordered liquid" be used; the term "liquid crystal" referring to low molecular weight compounds only. This argument has not been wholly implemented, and referring to polymeric mesophases as liquid crystalline is acceptable.[70]

Polymeric mesophases are in several ways similar to those of low molecular weight compounds. Depending on the degree and type of ordering, smectic, nematic and cholesteric phases are obtained.[15] Polymers as well as the low molecular weight mesogens can form one or more smectic phases, a nematic phase and an isotropic phase sequentially. In thermotropic syštems, the transitions are reversible and truly thermodynamic phases.

1.5.2 The Polymeric Nematic Phase

The quiescent nematic phase has the appearance of a turbid liquid (see Chapter 3, page 103). It transmits cross-polarised light, indicating an ordering within the system, which is confined to local domains as in the case of low molecular weight compounds. When sheared, the local domains are aligned, giving a relatively persistent anisotropy. The persistence depends on the temperature and the molecular weight of the polymer. For a chosen molecular weight, the higher the temperature, the shorter the period of anisotropy, *i.e.* the lower the persistence. The most characteristic feature of liquid crystalline melts or solutions, that occurs on shearing, is opalescence or

"shear whitening". This effect can be readily observed with the unaided eye and is a useful technique for establishing whether the polymer exhibits a liquid crystalline phase.

X-ray diffraction studies were carried out by De Vries[71] on low molecular weight compound mesophases. It was found that the nematic phase produced two diffuse rings; the inner ring corresponding to the length of the molecules, the outer ring corresponding to the interatomic distance between neighbouring molecules. In polymeric systems, the inner ring corresponds to the length of the repeat unit of the polymer, if the structure is regular.

CHAPTER 2

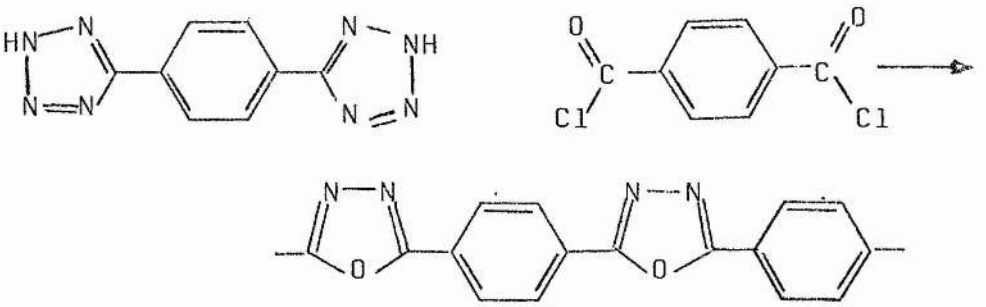
M O N O M E R S

2.1 OXADIAZOLE AND THIADIAZOLE CONTAINING POLYMERS

The oxadiazole and thiadiazole ring systems have been known for almost a century and have found uses in several important fields, such as the dye[72-74] and pharmaceutical industries.[75-79] It was however not until 1958 that Huisgen[80,81] and coworkers began to study their uses in polymers.

Abshire and Marvel[82] prepared, in 1961, a series of 12 polymers from bis-tetrazoles and diacid chlorides, (Scheme 10), based on the original reaction of Huisgen. These polymers were however of too low molecular weight for fibre production.

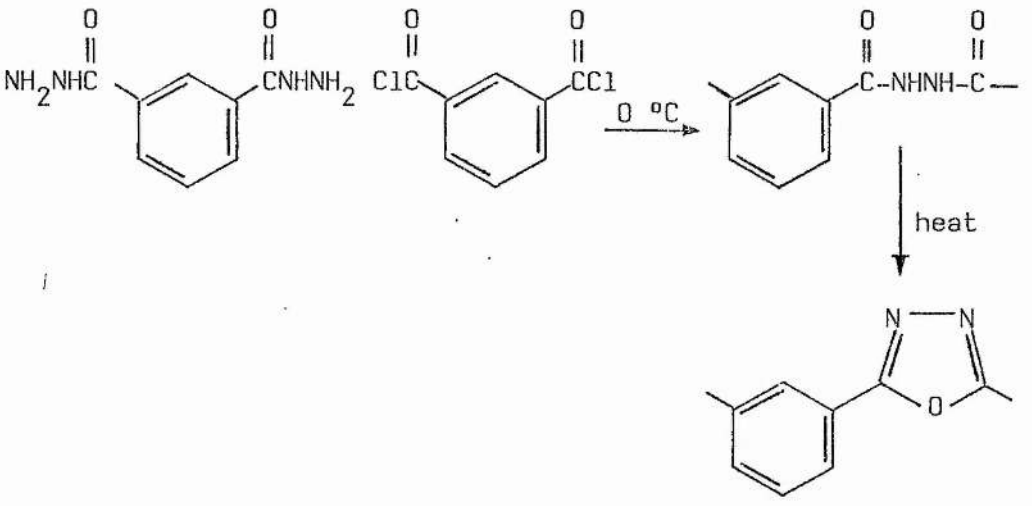
Scheme 10



In 1964, Frazer[83] and co-workers developed one of the most popular synthetic routes to polyoxadiazoles, through the cyclodehydration of polyhydrazides. The polyhydrazides were prepared by the low temperature solution polymerisation technique as developed by Frazer and Wallenberger, and were of high molecular weight. They also had the advantage of solubility in dipolar aprotic solvents such as dimethyl

sulphoxide and N,N-dimethylacetamide, and could thus be processed into fibres and films. These could then be converted by heat treatment to the more thermally stable oxadiazoles. (Scheme 11)

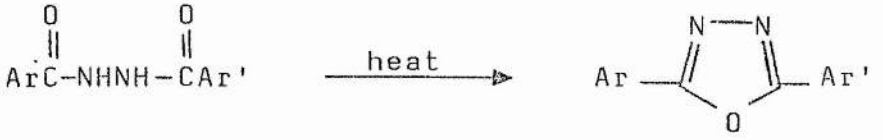
Scheme 11



The properties and uses of polymers based on 1,3,4--oxadiazoles have been investigated by the Furukawa Electric Company (Japan). The polymers are hydrolytically stable, partially crystalline and can be oriented to a higher degree of crystallinity by drawing. They are found to be more stable than polymers based on triazoles, but less stable than those based on thiadiazoles.

Poly-1,3,4-oxadiazoles can be prepared by a wide range of reactions, only two of which, (the most commonly used), will be discussed. The first method, already mentioned, is that used by Frazer and coworkers,[83] and is based on Stollé's[84] early observations on the cyclodehydration of diaroylhydrazines. (Scheme 12).

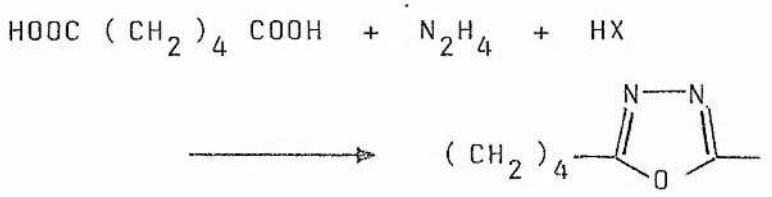
Scheme 12



Chemical dehydrating agents, such as phosphorus pentoxide, phosphorus pentachloride, oxalyl chloride, thionyl chloride, polyphosphoric acid and fuming sulphuric acid can also be used. However, thermal dehydration is chosen preferentially to these.

The second method, first used by Iwakura *et al*[85], is a one-step solution polymerisation by reaction of a dicarboxylic acid, or the corresponding nitrile, amide or ester, with hydrazine or its salts in polyphosphoric acid or fuming sulphuric acid. Reaction temperatures of 85 - 200 °C are usually employed and a 20 - 30% excess of hydrazine is often used, since this favours the formation of polymer of high molecular weight. (Scheme 13).

Scheme 13

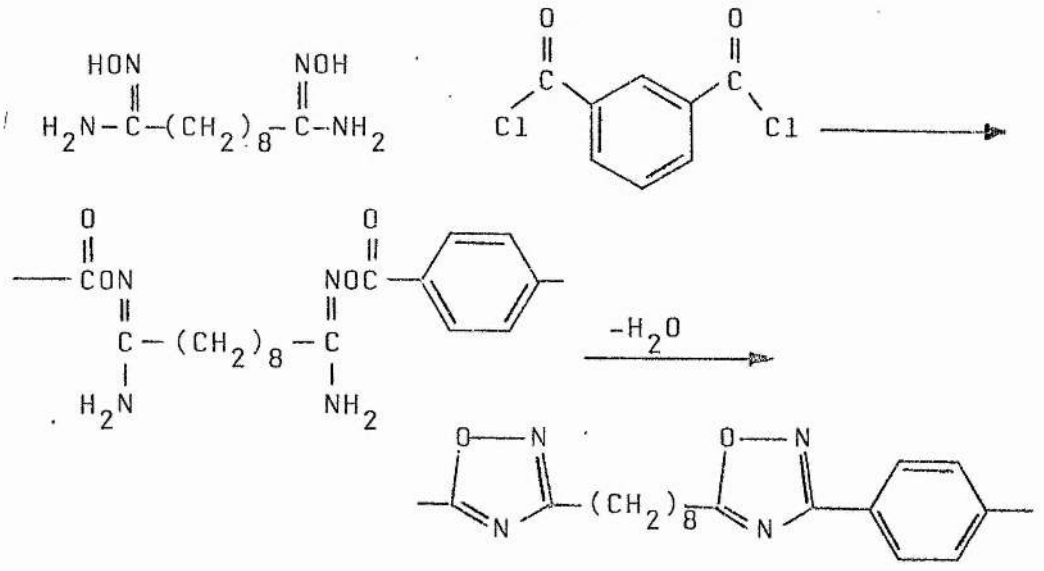


A larger number of poly-1,3,4-oxadiazoles have been made. They are most frequently used as films or fibres, produced from solutions of fuming sulphuric acid. They are flame-resistant and have favourable tensile properties. However, the other isomeric forms of the oxadiazole ring,

namely the 1,2,4- and 1,2,5- systems have received very little attention since the mid-sixties.

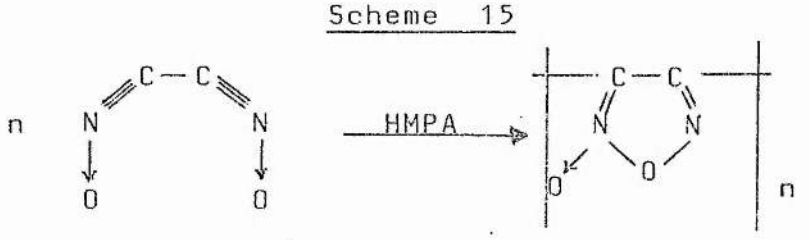
The most widely used synthesis of poly-1,2,4-oxadiazoles is the polymerisation of diamidoximes with diacid chlorides.[86] In many instances, the intermediate polyacylamidoxime can be isolated, and this on subsequent dehydration yields the polyoxadiazole. (Scheme 14).

Scheme 14



The polymerisation of nitrile oxides[87-89] yields poly--1,2,5-oxadiazoles. (Scheme 15). Two paths are possible however for the polymerisation of terephthalonitrile di-N-oxide.

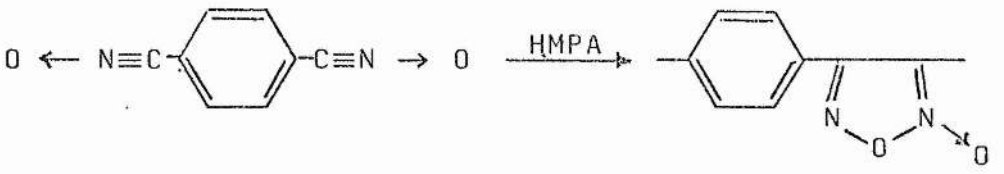
Scheme 15



In solution poly(1,2,5-oxadiazole N-oxides) are formed using

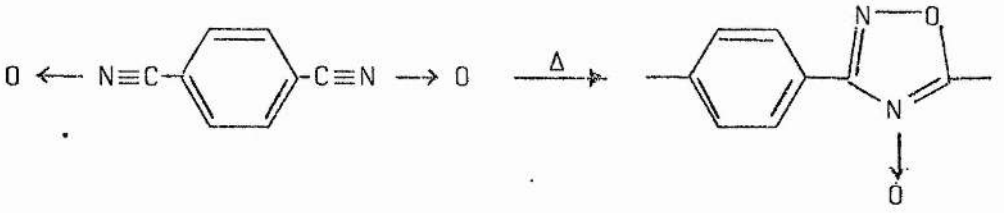
such solvents as dimethylacetamide, dioxan, hexamethylphosphoramide (HMPA) and dimethylformamide. Reactions can occur at ambient or low temperature. (Scheme 16).

Scheme 16



The solid state polymerisation of terephthalonitrile di-N--oxide, however, gives the poly(1,2,4-oxadiazole N-oxide). (Scheme 17).

Scheme 17

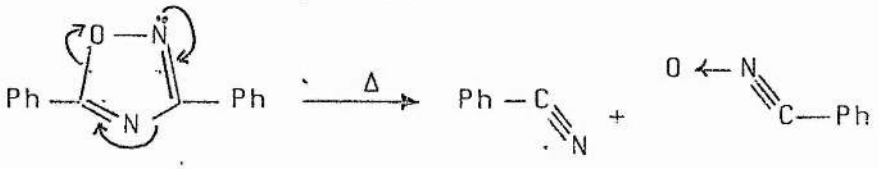


In terms of tractability and solubility, these polymers are quite similar to poly-1,3,4-oxadiazoles. However they possess considerably less thermal stability and have lower glass transition temperatures (Tg), than analogous 1,3,4--oxadiazole-based polymers.[90]

The reason for the difference in stability between the 1,3,4- and the 1,2,4-oxadiazole system has been shown to relate to the proportion of delocalisation energy, *i.e.* the 1,3,4-system is more stable as it has the higher delocalisation energy, as found from molecular orbital calculations. In addition, the 1,2,4-system can decompose by a retro-

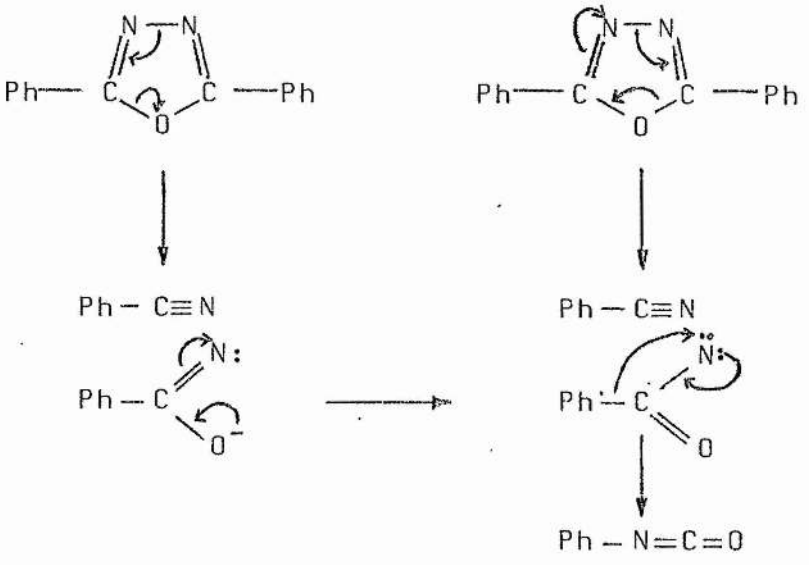
cycloaddition, to a nitrile and a nitrile oxide. (Scheme 18). More complex pathways are also possible. In the 1,3,4-system

Scheme 18



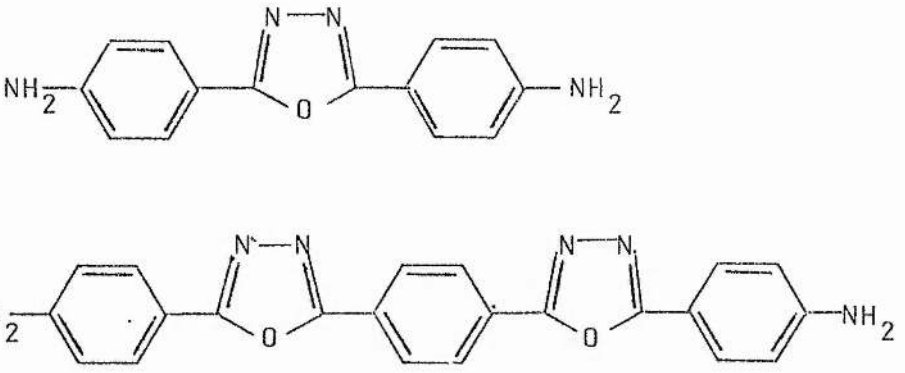
the ring also cleaves, but not until temperatures ~400 °C.[91] (Scheme 19). This lack of thermal stability is, no doubt, one of the reasons why the 1,2,4- and the 1,2,5- systems have been much less studied.

Scheme 19



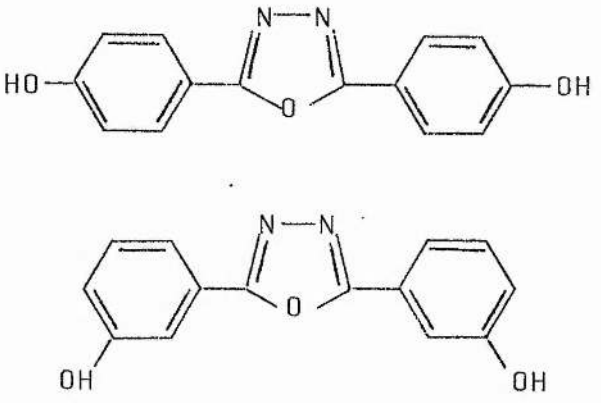
In the mid-sixties, Preston[92-94] prepared a range of polyamides based on the oxadiazole-containing diamines shown in Figure 20.

Figure 20



At the same time, Iwakura *et al*[95], published a paper detailing the preparation of two bisphenols containing a 1,3,4--oxadiazole ring. Polycarbonates were prepared by the transesterification of the bisphenols with diphenyl carbonate. Polyesters were prepared by reaction with diphenyl esters. The structures of the two bisphenols are shown in Figure 21.

Figure 21

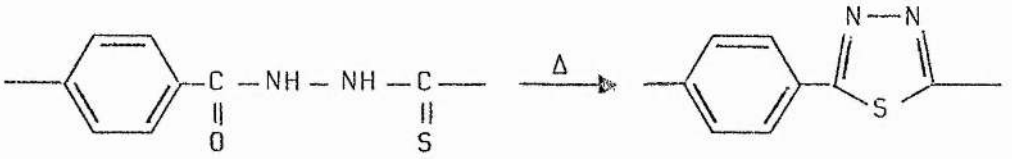


Oxadiazole-containing polymers with other functional groups have been prepared; amide and imide functional groups by Bruma *et al*[96] and ether functional groups by Steinmann.[97]

Of the three isomeric forms of thiadiazole, only two, the 1,3,4- and the 1,2,5- forms have been used in polymers. Thiadiazole-containing polymers have received less attention than the oxadiazole-containing polymers, not because their properties are inferior, (for they are indeed not), but for the reason that thiadiazole precursors are less accessible.

Poly-1,3,4-thiadiazole fibres have been prepared in a manner analogous to that of poly-1,3,4-oxadiazoles - the cyclodehydration of a polyoxythiahydrazide fibre. (Scheme 20). This cyclisation occurs at lower temperatures and at

Scheme 20



a faster rate than the corresponding cyclisation to oxadiazoles. Fabrication of the polyoxythiahydrazide is easy, due to its high solubility in pyridine and dimethylacetamide.

Thiadiazole-containing polymers exhibit the same desired chemical and thermal stability as oxadiazoles, but they are somewhat more tractable.

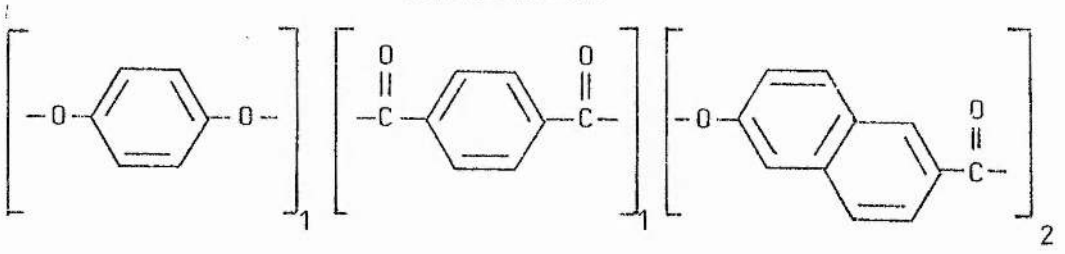
Various patents and papers have been published, which describe thiadiazole-containing polymers and the fibres obtained from these polymers.[98,99] The main uses of these polymers are as packing materials, high strength fibres and electrical insulators.[100]

2.2. THE AIM AND SCOPE OF THE PROJECT

2.2.1 The Aim of the Project

The work described in this thesis arose from a suggestion by Dr. W. A. MacDonald, of I.C.I. New Science Group, who was interested in the formation of novel co-polyesters for fabrication into high strength, high modulus fibres. One potentially useful polymer prepared at that time by I.C.I. had the composition shown in Figure 22. Referred to as Po in this project, it was prepared by the

Figure 22

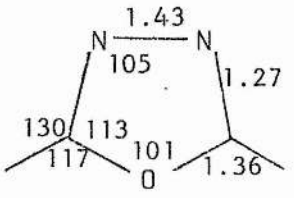


process of melt trans-esterification using the phenolic acetates. (Chapter 1, page 34). Due to the fact that it is composed of mesogenic rigid-rod units, it requires a high temperature (~380 °C, see Chapter 4), for its fabrication into fibres. Even at these temperatures, however, some degradation may occur, resulting in fibres with reduced strength. It was thus the intention to produce a range of copolyesters with lower processing temperatures by replacing all, or some, of one or more of the units in P_o, using angular disrupting units based on the 1,3,4-oxadiazole and the 1,3,4-thiadiazole structures. These two units were selected for their high thermal stability and because

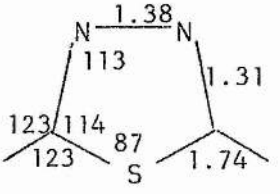
previous polymers containing these units could be used to produce fibres with desirable properties. (Section 2.1).

Duc to the different geometries of the oxadiazole and thiadiazole systems, the angle, α, between the "chain--continuing" bonds of the two rings is different. The thiadiazole has a less disruptive effect on the linearity of the polymers. (Figure 23).

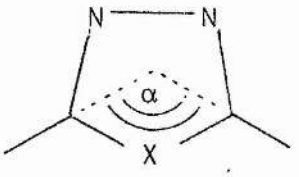
Figure 23



ref.101



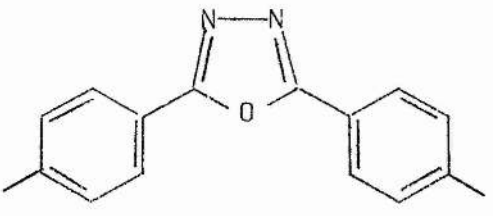
ref.102



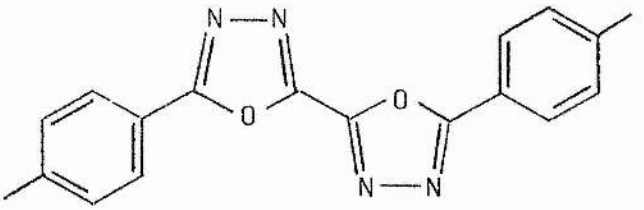
when X = O, α = 133
when X = S, α = 159

The monomers based on these angular systems can be divided into three main structural types (I, II and III), which are shown in Figure 24.

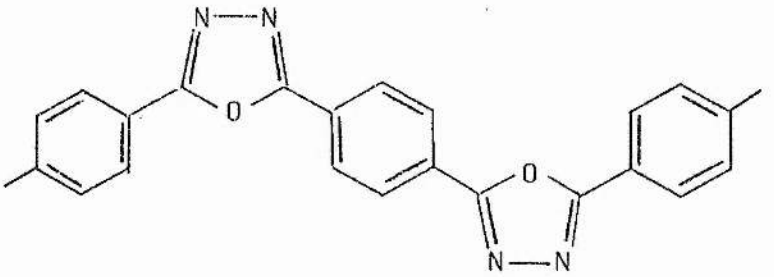
Figure 24



I



II



III

Structure I produces a definite bending in any polymer chain and is thus non-mesogenic, whereas the geometrical arrangement of the two oxadiazole rings in structures II and III can produce a conformation in which the chain-continuing bonds are parallel and oppositely directing, as the angular element of one ring effectively cancels that of the second ring.

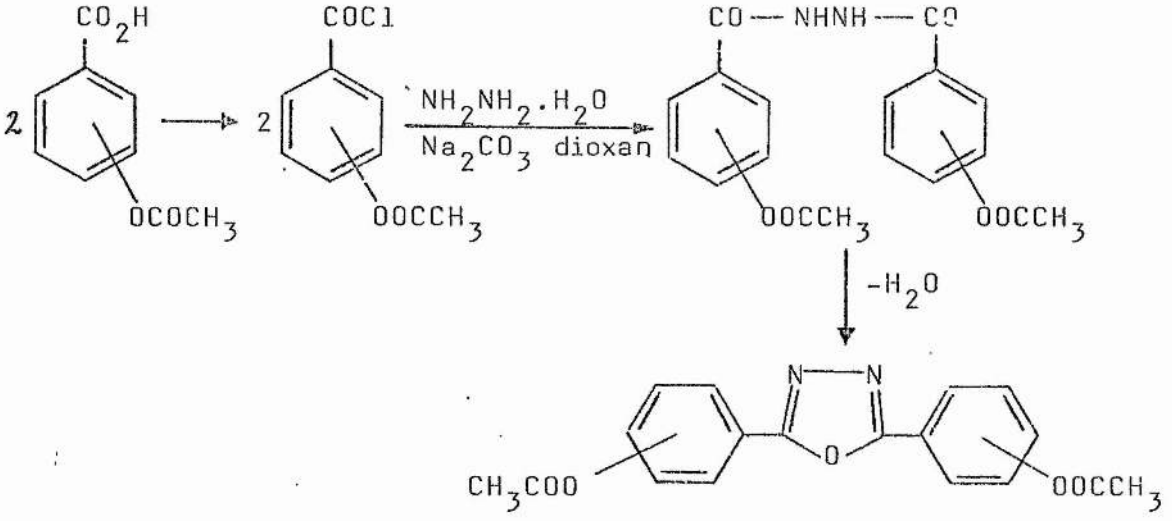
2.2.2 Synthesis of the Monomers

Oxadiazoles

The symmetrical diacetates [95] and dicarboxylic acids[103] based on structure I were already known. The diacetates were prepared by the low temperature reaction of two molar equivalents of the acetoxybenzoyl chloride with a molar equivalent of hydrazine monohydrate and dehydration of the resulting diaroylhydrazine with thionyl chloride (Scheme 21) Acylation of the hydroxybenzoic acid is necessary prior to its conversion to the acid chloride, otherwise self-

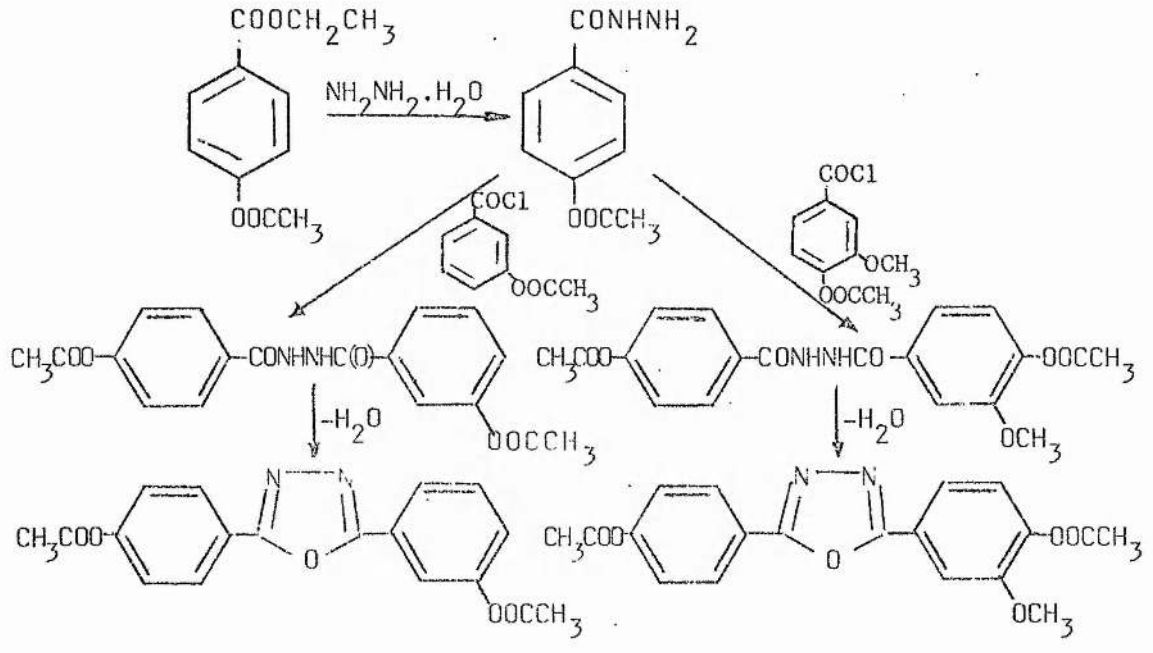
polymerisation of the acid occurs.

Scheme 21



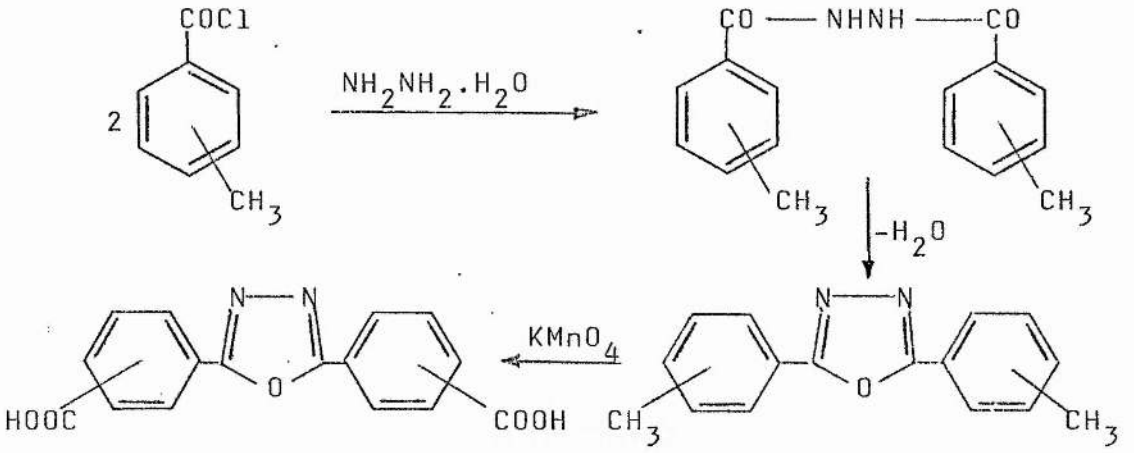
Two unsymmetrical diacetates based on structure I were prepared *via* unsymmetrical diaroylhydrazines, which were themselves prepared from an aroylhydrazine and an acid chloride. The aroylhydrazine was prepared from the ethyl ester by the method used by Struvé and Radenhausen.[104] (Scheme 22).

Scheme 22



The symmetrical dicarboxylic acids of structure I were prepared by the method of Javaid and Smith,[103] *i.e.* by the oxidation of the corresponding di-tolyl-oxadiazoles using potassium permanganate. (Scheme 23).

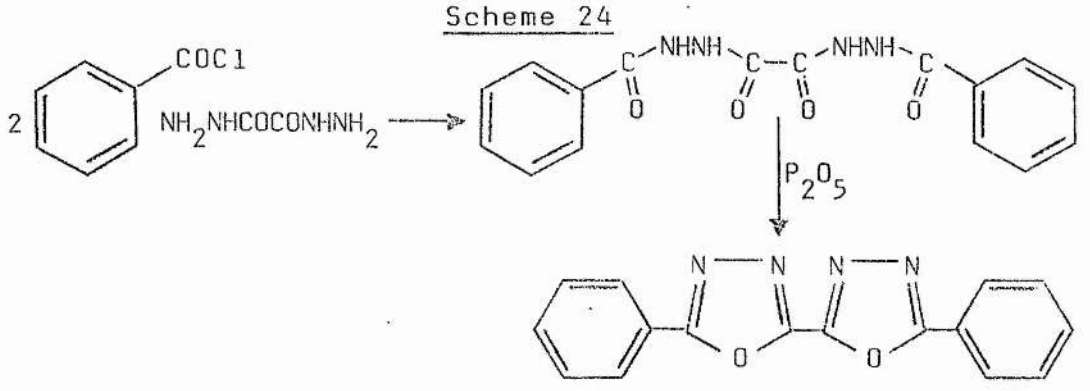
Scheme 23



Initial polymer work at this stage indicated that those polymers containing the oxadiazole-based diacids have less desirable properties than those of polymers containing the oxadiazole-based diacetates. Therefore, further synthetic work on the diacids was not undertaken.

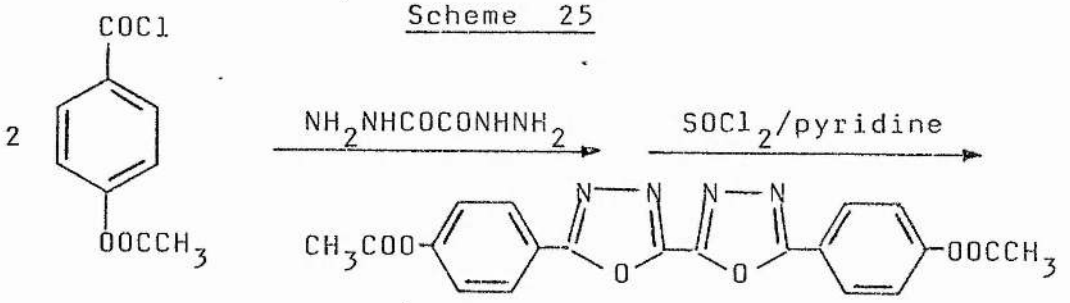
The parent compound with structure II, 5,5'-diphenyl--bis-(1,3,4-oxadiazole)-2;2'-diyl, was prepared in 1904 by Stollé and Münch,[105] by the method shown in scheme 24.

Scheme 24



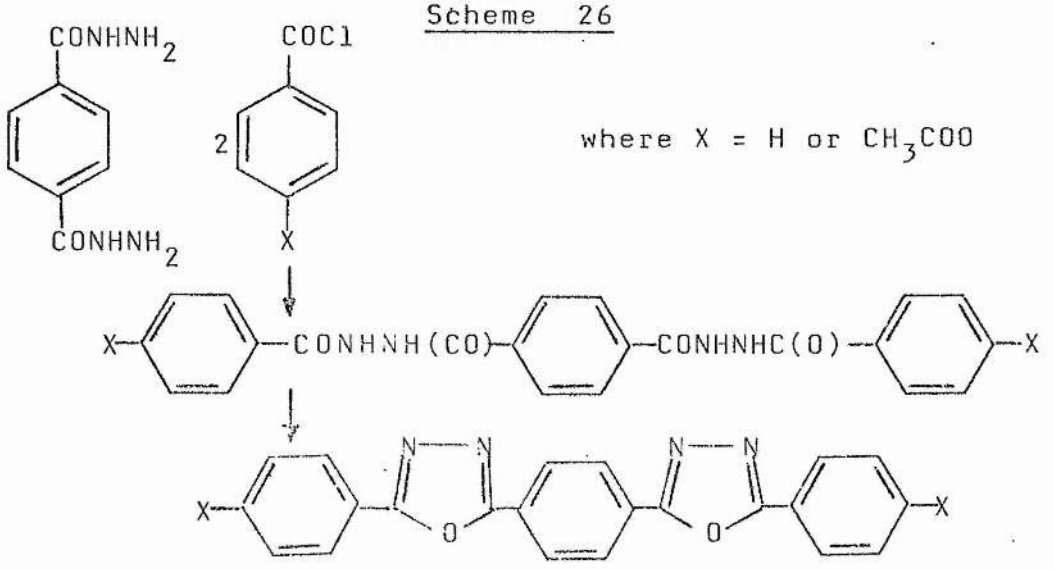
It was found, however, that thionyl chloride/pyridine could also be used to bring about the cyclodehydration of the dihydrazide and the diacetoxy-compound was prepared by this method using *p*-acetoxybenzoyl chloride. (Scheme 25).

Scheme 25



Several literature methods are available for the synthesis of compounds containing structure III.[106-108] The method used here was analogous to that used for the preparation of monomers with structures I and II. This involved the low-temperature reaction of terephthaloyl or isophthaloyl dihydrazide with benzoyl or *p*-acetoxybenzoyl chloride, with subsequent cyclodehydration to give the unsubstituted or diacetoxy compounds (Scheme 26, using terephthaloyl hydrazide).

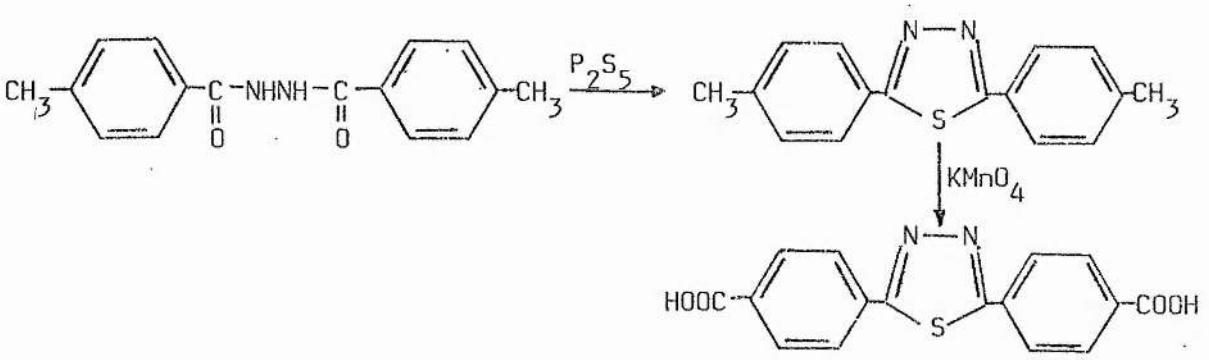
Scheme 26



Thiadiazoles

The diacids with structure I were prepared by the method of Javaid and Smith.[103] In this method, the bis-toluoyl-hydrazines were converted to the thiadiazoles by heating with phosphorus pentasulphide in xylene. These tolyl-thiadiazoles were then oxidised to the dicarboxylic acids with potassium permanganate. (Scheme 27).

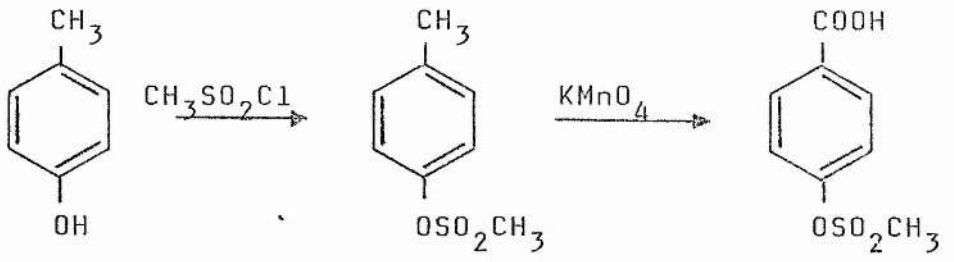
Scheme 27



This method, however, failed for the preparation of the diacetates. The acetoxy-groups reacted with the phosphorus pentasulphide to give a mixture of products, as shown by thin layer chromatography. An alternative protecting group for the hydroxyl-function was therefore sought.

The group chosen was the mesyl(methylsulphonyl) group. However, the mesylation of *p*-hydroxybenzoic acid cannot be carried out directly, as this results in the formation of a polymer.[109] Thus an indirect method was used; *p*-cresol was mesylated and the subsequent oxidation of the methyl group with permanganate gave *p*-mesyloxybenzoic acid. (Scheme 28). The acid chloride was then prepared and by reaction with hydrazine monohydrate the diaroylhydrazine was obtained.

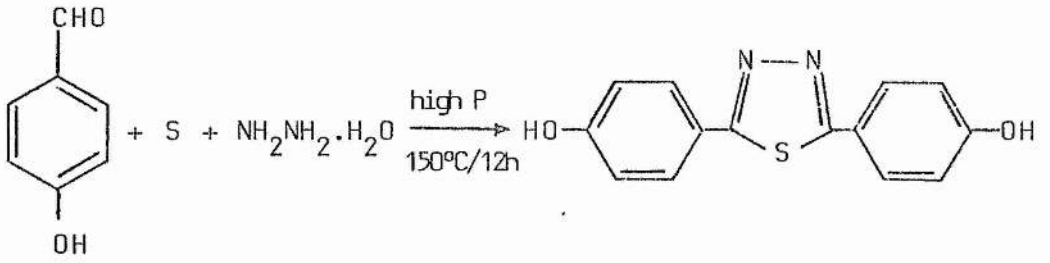
Scheme 28



This, however, once again gave a mixture of products on reaction with phosphorus pentasulphide.

Another alternative synthesis was sought. The literature method which appeared simplest on paper[110] (Scheme 29)

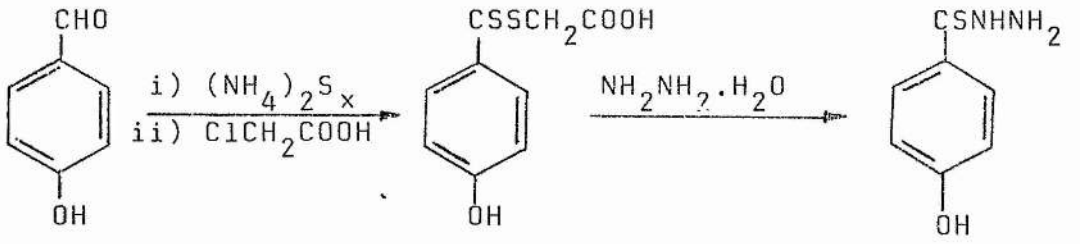
Scheme 29



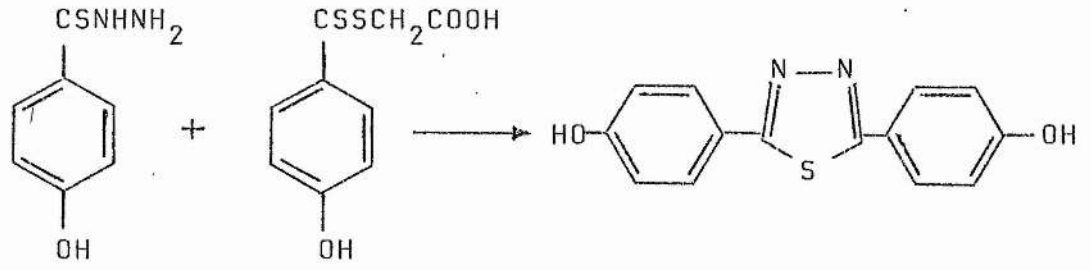
was considered impracticable on a large scale because of lack of suitable equipment and difficulty in removing the hydrogen sulphide by-product.

The second literature synthesis[111] (Scheme 30) proved unsatisfactory. In the first stage, the yield was only 7%, whereas the authors claimed 32%; and although the second stage was reproducible, in the final stage the yield was again much lower (26%) than that claimed (75%).

Scheme 30



Then:



This is an aspect of the work which still remains to be explored.

FOREWORD TO 2.3

Materials and Apparatus

Melting points were determined in open capillaries and are uncorrected. Those greater than 300 °C were determined by differential scanning calorimetry (D.S.C.). Infrared spectra were recorded for Nujol mulls using sodium chloride cells on a Perkin-Elmer 1310 IR spectrophotometer. Proton spectra were recorded at 80 MHz on a Bruker-WP80 Fourier transform spectrometer for 10% solutions with tetramethylsilane as internal reference. Mass spectra were obtained on an AEI MS-902 spectrometer operating at 70 eV with a source

temperature of 200 °C. Samples were introduced by means of a direct insertion probe.

Abbreviations

s,	singlet
m,	multiplet
br,	broad
b.p.,	boiling point
m.p.,	melting point
DMF,	dimethylformamide
petroleum,	petroleum b.p. 40/60 °C

2.3 EXPERIMENTAL

2.3.1 Acetylation of Phenolic Functions

p-Acetoxybenzoic acid. *p*-Hydroxybenzoic acid (100 g, 0.723 mol.) and acetic anhydride (300 ml) were heated under reflux for 4 h. The product which crystallised from the cooled solution was recrystallised twice from chloroform giving small, white needles, m.p. 194 °C (lit.[112] 191-192 °C); yield 123.7 g (95%).

m-Acetoxybenzoic acid was similarly prepared from *m*-hydroxybenzoic acid (100 g). However the product did not crystallise on cooling, and was obtained by pouring the solution into water (1,000 ml) and triturating for several minutes. It was washed exhaustively with water, dried *in vacuo* over P_2O_5, and after two recrystallisations from benzene/petroleum (70:30) was obtained as small, white cubes, m.p. 128 °C (lit.[112] 127-129 °C); yield 108.3 g (83%).

p-Acetoxy-m-methoxybenzoic acid was prepared from *p*-hydroxy--*m*-methoxybenzoic acid (50 g) by the method used to prepare m-acetoxybenzoic acid. Recrystallisation from the minimum quantity of ethanol produced small, white prisms, m.p. 142 °C (lit.[113] 142 °C); yield 54.4 g (88%).

2,7-Diacetoxynaphthalene was similarly prepared from 2,7--dihydroxynaphthalene (50 g). Recrystallisation from ethanol gave delicate, lustrous leaves, m.p. 127 - 129 °C (lit.[114] 129 °C); yield 74.3 g (97%)

1,5-Diacetoxynaphthalene was prepared in exactly the same way from 1,5-dihydroxynaphthalene. Recrystallisation from benzene gave large, pale yellow prisms, m.p. 157 - 159 °C (lit.[115] 159-160 °C); yield 60.0 g (79%).

6-Acetoxy-2-naphthoic acid was provided by I.C.I., to whom we express our thanks.

2.3.2 Formation of Acid Chlorides

p-Acetoxybenzoyl chloride was prepared by heating *p*-acetoxybenzoic acid (100 g) under reflux in thionyl chloride (300 ml) for 2 h. The excess thionyl chloride was removed by distillation at reduced pressure - the last portion being co-distilled with benzene - to yield a white slurry. This after distillation (b.p. 77 °C/0.05 mmHg) gave a white, crystalline solid, m.p. 30 °C (lit.[116] 30 °C); yield 89.9 g (82%).

m-Acetoxybenzoyl chloride, b.p. 102 °C/1.5 mmHg (lit.[116] 155 °C/16 mmHg), was similarly prepared in 84% yield from

m-acetoxybenzoic acid (100 g).

p-Acetoxy-*m*-methoxybenzoyl chloride was similarly prepared from *p*-acetoxy-m-methoxybenzoic acid (50 g); after two recrystallisations from chloroform it gave large, light-green plates, m.p. 57 °C (lit.[117] 57 °C); yield 45.4 g (83%).

6-Acetoxy-2-naphthoyl chloride was similarly prepared from 6-acetoxy-2-naphthoic acid (100 g.) Recrystallisation from carbon tetrachloride gave light-brown prisms, m.p. 121 °C (lit.[118] 124 °C); yield 89.0 g (82%).

p-Toluoyl chloride was prepared similarly from *p*-toluic acid (100 g), b.p. 64 °C/0.1 mmHg (lit.[119] 225-227 °C); yield 84.5 g (74%).

m-Toluoyl chloride was prepared in exactly the same way. b.p. 41 °C/0.2 mmHg (lit.[120] 86 °C/5 mmHg); yield 90.4 g (79%).

2.3.3 Formation of Ethyl Esters

Ethyl *p*-hydroxybenzoate was prepared by heating *p*-hydroxybenzoic acid (100 g) under reflux in ethanol (300 ml) containing concentrated sulphuric acid (1 ml) for 4 h. Most of the ethanol was then distilled off at reduced pressure, and the mixture then added to water (1,000 ml). The precipitated ester was filtered off, washed with water, and dried *in vacuo* over phosphorus pentoxide. The ester was precipitated from an ethanolic solution by the addition of petroleum, m.p. 112 °C (lit.[121] 112 °C); yield 115.5 g (96%).

Diethyl terephthalate. A suspension of terephthalic acid (50 g) in ethanol (1,000 ml), saturated with hydrogen chloride gas, was heated under reflux for 6 h and then left to cool overnight. The product (long needles) was filtered off, and a second crop obtained by dilution of the filtrate with water; recrystallised from ethanol/water (90:10), the ester had m.p. 44 °C (lit.[122] 44-46 °C); yield 60.3 g (89%).

2.3.4 Formation of Hydrazides

2.3.4.1 *Formation of Hydrazides from Ethyl Esters*

p-Hydroxybenzoylhydrazine was prepared by heating ethyl p-hydroxybenzoate (33.2 g, 0.2 mol.) with hydrazine hydrate (15 g, 14.6 ml, 0.3 mol.) directly, for 2 h at reflux. On heating, solution was quickly achieved, and approximately thirty minutes later, product began to precipitate. After 2 h the reaction was assumed to be complete; the mixture by this stage was almost totally solid. The solid was washed with water (500 ml) and recrystallised from DMF as small, white needles, m.p. 257 °C (lit.[104] 260 °C); yield 26.3 g (87%).

Terephthaloyl dihydrazide (with I. W. Harvey). - Diethyl terephthalate (61.2 g, 0.27 mol.) was dissolved in hot ethanol (*ca.* 40 ml). To this was added hydrazine monohydrate (27.7 g, 27 ml, 0.55 mol.) and the resultant solution was heated under reflux for 4 h. After 5 min. the solution turned pale yellow and after *ca.* 40 min., the product began to precipitate. Once cool, the paste formed was filtered, washed with 800 ml of boiling ethanol and dried at 100 °C.

The product was assumed to be pure: m.p. 350 °C (lit.[123] > 300 °C); yield 49.2 g (94%).

2.3.4.2 *Formation of Symmetrical Diacylated Hyrazines*

1,2-Bis(*p*-acetoxybenzoyl)hydrazine. *p*-Acetoxybenzoyl chloride (79.4 g, 0.4 mol) in dioxan (100 ml) was added dropwise and with good mechanical stirring to a suspension of hydrazine monohydrate (10.0 g, 9.7 ml, 0.2 mol.) and sodium carbonate (21.2 g, 0.2 mol.) in dioxan (50 ml), so that the temperature of the mixture was maintained between 3 - 7 °C. Once the addition was complete, stirring was continued for a further 3 h at this temperature and then for a further 3 h at room temperature. The resultant slurry was added, with stirring, to water (1,000 ml), and the product filtered off, washed with water (1,000 ml), saturated sodium hydrogen carbonate (500 ml), and again with water (1,000 ml). Recrystallisation from methanol yielded small, fine, white needles, m.p. 245 - 246 °c (lit.[89] 247.5 °C); yield 40.1 g (56%).

1,2-Bis(*m*-acetoxybenzoyl)hydrazine formed in a similar manner, recrystallised from methanol as white plates, m.p. 147 - 148 °C (lit.[89] 149.5 - 150.0 °C); yield 34.9 g (49%).

1,2-Bis(6-acetoxy-2-naphthoyl)hydrazine prepared similarly, recrystallised from DMF as small, white needles, m.p. 246 - 248 °C; yield 23.1 g (51%). (Found: C, 68.2; H, 4.3; N, 6.0. $C_{26}H_{20}N_2O_6$ requires C, 68.4; H, 4.4; N, 6.1%.) $\nu_{max.}$ 3220 (NH), 1755 (CO, OAc), 1590, 910 and 725 cm^{-1}; δ_H (DMSO-d6) 2.35 (6H, s, CH_3), 7.25 - 8.75 (12H, m, Ar-H),

10.70 (2H, br s, NH); *m/z* 456 (M^+), 438, 414, 398 and 354.

1,2-Di-*p*-toluoylhydrazine, prepared in the same way, recrystallised as small, white needles from ethanol, m.p. 249 - 251 °C (lit.[124] 253 - 254 °C); yield 38.0 g (57%).

1,2-Di-*m*-toluoylhydrazine was similarly prepared, yielding white needles from ethanol, m.p. 216 - 217 °C (lit.[125] 214 - 216 °C); yield 33.1 g (49%).

2.3.4.3 *Formation of Unsymmetrical Diacylated Hydrazines*

1-(*m*-Acetoxybenzoyl)-2-(*p*-hydroxybenzoyl)hydrazine was prepared by the dropwise addition of a solution of *m*-acetoxybenzoyl chloride (19.85 g, 0.1 mol.) in dioxan (30 ml), to a well-stirred suspension of *p*-hydroxybenzoylhydrazine (15.2 g, 0.1 mol.) and sodium carbonate (5.3 g, 0.05 mol.) in dioxan (60 ml) at room temperature. Stirring was continued for 4 h after which the hydrazide was collected in the usual manner. Recrystallisation from DMF gave small, white needles, m.p. 185 °C; yield 16.3 g (52%). It was converted without further purification into 1-(*m*-acetoxybenzoyl)-2-(*p*-acetoxybenzoyl)hydrazine, which on recrystallisation from methanol gave small, white needles, m.p. 160°; yield 84%. (Found: C, 60.4; H, 4.4; N, 7.8. $C_{18}H_{16}N_2O_6$ requires C, 60.7; H, 4.5; N, 7.9%.) $\nu_{max.}$ 3170 (NH), 1745 (CO), 1595 and 1565 cm^{-1}; δ_H ($(CD_3)_2CO$) 2.38 (6H, s, CH_3), 7.50 - 8.50 (8H, m, Ar-H); *m/z* 356 (M^+), 298, 254, 236, 194, 176.

1-(*p*-Acetoxy-*m*-methoxybenzoyl)-2-(*p*-hydroxybenzoyl)hydrazine was similarly prepared from *p*-acetoxy-*m*-methoxybenzoyl chloride

and *p*-hydroxybenzoylhydrazine and recrystallised from DMF as white needles, with m.p. 155 °C; yield 32.5 (47%). This was again acetylated to 1-(*p*-acetoxy-*m*-methoxybenzoyl)-2--(*p*-acetoxybenzoyl)hydrazine. Recrystallisation from methanol gave small, white needles, m.p. 144 - 145 °C; yield 27.6 g (80%). (Found: C, 59.1; H, 4.7; N, 7.3. $C_{19}H_{18}N_2O_7$ requires C, 59.1; H, 4.7; N, 7.3%); $\nu_{max.}$ 3175 (NH), 1750 (CO), 1585, 1565, 1215 cm^{-1}; δ_H (DMSO-d_6) 2.33 (6H, s, CH_3), 3.93 (3H, s, CH_3O), 7.25 - 8.25 (7H, m, Ar-H), 10.70 (2H, br s, NH); *m/z* (M^+ absent), 355, 326, 314, 284, 254.

2.3.4.4 *Formation of the Dihydrazides*

Oxalyl bis(2-benzoyl)hydrazide. Benzoyl chloride (2.81 g, 2.3 ml, 0.02 mol.) in dioxan (10 ml) was added dropwise with stirring to a suspension of oxalyl dihydrazide (1.18 g, 0.01 mol.) and sodium carbonate (1.06 g, 0.01 mol.) in dioxan (25 ml). The mixture was stirred for 2 h at room temperature and left overnight. The dihydrazide on recrystallisation from DMF gave small, white needles, m.p. 275 °C (lit.[126] 278 °C); yield 1.85 g (57%).

Oxalyl bis[2-(*p*-acetoxybenzoyl)]hydrazide (with T. Bowen). This was similarly prepared using *p*-acetoxybenzoyl chloride (24 g, 0.17 mol.). Attempted recrystallisation from DMF gave a white powder, m.p. 261 °C; yield 23.0 g (61%). (Found: C, 53.8; H, 4.3; N 12.6. $C_{20}H_{18}N_4O_8$ requires C, 54.3; H, 4.1; N, 12.7%); $\nu_{max.}$ 3200 (NH), 1750 (CO), 1700, 1240 cm^{-1}; δ_H (DMSO-d_6) 2.33 (6H, s, CH_3), 7.32 and 7.95 (8H, AA'BB' pattern, Ar-H), 10.55 (4H, s, NH); *m/z* (M^+,

absent), 206, 178, 164, 163, 162, 137.

Isophthaloyl bis(2-benzoyl)hydrazide, (with T. Bowen). This was prepared by the normal procedure from isophthaloyl dihydrazide (1.94 g, 0.01 mol.) and sodium carbonate (1.06 g, 0.01 mol.) in dioxan (10 ml) and benzoyl chloride (2.81 g, 0.02 mol.). Recrystallisation from acetic acid gave white flakes, m.p. 296 - 298 °C (lit.[127] 291 °C); yield 2.37 (59%).

Terephthaloyl bis(2-benzoyl)hydrazide, (with I. W. Harvey). This was prepared similarly from terephthaloyl dihydrazide. Recrystallisation from DMF gave small, white needles, m.p. 332 - 334 °C (lit.[128] 336 - 338 °C); yield 1.53 g (38%).

Isophthaloyl bis [2-(*p*-acetoxybenzoyl)]hydrazide,(with T. Bowen). This was similarly prepared from isophthaloyl dihydrazide (9.95 g, 0.05 mol.), sodium carbonate (5.4 g, 0.05 mol.) and *p*-acetoxybenzoyl chloride (20.36 g, 0.10 mol.). Due to its insolubility it was obtained impure and used without purification in the next stage, m.p. 302 - 303 °C; yield 17.5 g (66%). (Found: C, 58.9; H, 4.2; N, 10.7. $C_{26}H_{22}N_4O_8$ requires C, 60.2; H, 4.3; N, 10.8%); $\nu_{max.}$ 3190 (NH), 1740 (CO), 1675, 1635 cm^{-1}; (No N.M.R. - too insoluble); *m/z* (M^+, absent), 121, 57, 55, 44.

Terephthaloyl bis[2-(*p*-acetoxybenzoyl)]hydrazide,(with I. W. Harvey). This was prepared in the same manner using terephthaloyl dihydrazide. The dihydrazide produced was too insoluble in all solvents to be recrystallised. It had m.p. 308 - 309 °C (pale brown powder); yield 12 g (from 7.5 g of terephthaloyl dihydrazide). $\nu_{max.}$ 3180 (NH),

1750 (CO), 1590, 1540.

2.3.5 The Cyclodehydration of Hydrazides to 1,3,4-Oxadiazoles

All the oxadiazoles in this work were prepared by heating the hydrazide in thionyl chloride/pyridine (98:2) for 2 h under reflux. The excess thionyl chloride and the pyridine were removed by distillation at reduced pressure to give the crude products.

2,5-Bis-(*p*-acetoxyphenyl)-1,3,4-oxadiazole was prepared from 1,2-bis(p-acetoxybenzoyl)hydrazine (30 g). Two recrystallisations from acetone gave white needles, m.p. 206 °C (lit.[89] 206 °C); yield 21.5 g (75%).

2,5-Bis(*p*-acetoxyphenyl)-1,3,4-oxadiazole, from 1,2-bis(m--acetoxybenzoyl)hydrazine, was obtained as white cubes from acetone, m.p. 159 - 160 °C (lit.[89] 159.5 - 160.5 °C); yield 13.4 g (47%).

2,5-Bis(6-acetoxy-2-naphthyl)-1,3,4-oxadiazole, prepared from 1,2-bis(6-acetoxy-2-naphthoyl)hydrazine (20 g), was recrystallised from DMF as cream coloured needles, m.p. 229 - 230 °C; yield 9.0 g (47%). (Found: C, 71.0; H, 4.2; N, 6.5. $C_{26}H_{18}N_2O_5$ requires C, 71.2; H, 4.1; N, 6.4%); $\nu_{max.}$ 1755 (CO), 1245, 970, 910, 895, 820 cm^{-1}; δ_H ($CDCl_3$) 2.38 (6H, s, CH_3), 7.25 - 8.75 (12H, m, Ar-H); *m/z* 438 (M^+), 398, 354, 297, 281.

2,5-Di-*p*-tolyl-1,3,4-oxadiazole, prepared from 1,2-di-*p*--toluoylhydrazine (35.0 g) gave white needles from acetone, m.p. 173 °C (lit.[125] 175 °C); yield 26.6 g (81%).

2,5-Di-*m*-tolyl-1,3,4-oxadiazole, prepared from 1,2-di-*m*-toluoylhydrazine (30.0 g), gave white needles from petroleum, m.p. 77 °C (lit.[125] 72 °C); yield 20.3 g (72%).

2-(*m*-Acetoxyphenyl)-5-(*p*-acetoxyphenyl)-1,3,4-oxadiazole, prepared from 1-(*m*-acetoxybenzoyl)-2-(*p*-acetoxybenzoyl)-hydrazine (15 g), was recrystallised as white cubes from acetone, m.p. 195 °C; yield 9.8 g (69%). (Found: C, 63.6; H, 4.1; N, 8.3. $C_{18}H_{14}N_2O_5$ requires C, 63.9; H, 4.2; N, 8.3%); $\nu_{max.}$ 1745 (CO), 1195, 1010, 960, 920 cm^{-1}; δ_H(DMSO-d_6) 2.38 (6H, s, CH_3), 7.50 - 8.50 (8H, m, Ar-H); *m/z* 338 (M^+), 296, 254, 226, 197.

2-(*p*-Acetoxy-*m*-methoxyphenyl)-5-(*p*-acetoxyphenyl)-1,3,4-oxadiazole, prepared from 1-(*p*-acetoxy-*m*-methoxybenzoyl)-5-(*p*-acetoxybenzoyl)hydrazine (25 g) gave small, white needles from acetone, m.p. 166 - 168 °C; yield 9.7 g (42%). (Found: C, 61.6; H, 4.3; N, 7.6. $C_{19}H_{16}N_2O_6$ requires C, 61.8; H, 4.4; N, 7.6%); $\nu_{max.}$ 1735 (CO), 1580, 1170, 995, 960 cm^{-1}; δ_H ($CDCl_3$) 2.38 (6H, s, CH_3), 4.00 (3H, s, CH_3O), 7.25 - 8.00 (7H, m, Ar-H); *m/z* 368 (M^+), 326, 284, 151, 121.

2,2'-Bis(5-phenyl-1,3,4-oxadiazolyl) prepared from oxalyl bis(2-benzoyl)hydrazine (1 g) gave fine, white needles from DMF, m.p. 271 - 273 °C (lit.[105] 270 °C); yield 0.31 g (35%).

2,2'-Bis[5-(*p*-acetoxyphenyl)-1,3,4-oxadiazolyl] (with T. Bowen). Prepared from oxalyl bis[2-(*p*-acetoxybenzoyl)]hydrazide (19 g), this gave white needles from DMF, m.p. 285 - 286 °C; yield 11.5 g (66%). (Found: C, 59.1; H, 3.5; N, 13.8. $C_{20}H_{14}N_4O_6$ requires C, 59.1; H, 3.4; N, 13.8%); $\nu_{max.}$

1740 (CO), 1600, 1190 cm^{-1}; δ_H (DMSO-d_6) 2.35 (6H, s, CH_3), 7.42 and 8.25 (8H, d d, Ar-H); *m/z* 406 (M^+), 364, 322, 161, 122.

1,3-Bis(5-phenyl-1,3,4-oxadiazol-2-yl)benzene, (with T. Bowen). This, prepared from isophthaloyl bis(2-benzoyl)hydrazide (1 g), gave white flakes from acetic acid, m.p. 248 - 250 °C (lit.[129] 237 - 239 °C); yield 0.57 g (63%).

1,4-Bis(5-phenyl-1,3,4-oxadiazol-2-yl)benzene, (with T. Bowen). This, prepared from terephthaloyl bis(2-benzoyl)hydrazide (0.5 g), gave white needles from DMF, m.p. 288 - 290 °C (lit.[129] 311 - 313 °C); yield 0.5 g (55%).

1,3-Bis[5-(*p*-acetoxyphenyl)-1,3,4-oxadiazol-2-yl]benzene, (with T. Bowen). This, prepared from isophthaloyl bis[2-(*p*-acetoxybenzoyl)]hydrazide (17.4 g), gave pale brown flakes from acetic acid, m.p. 294 - 296 °C; yield 7.8 g (48%). (Found: C, 64.3; H, 3.8; N, 11.3. $C_{26}H_{18}N_4O_6$ requires C, 64.7; H, 3.8; N, 11.6%); $\nu_{max.}$ 1750 (CO), 1590, 960 cm^{-1}; ^1H n.m.r. not available because of low solubility; *m/z* 482 (M^+), 440, 398, 265, 249, 209.

1,4-Bis[5-(*p*-acetoxyphenyl)-1,3,4-oxadiazol-2-yl]benzene, (with I. W. Harvey). Prepared from terephthaloyl bis[2-(*p*-acetoxybenzoyl)]hydrazide (crude, 12 g), this was recrystallised from DMF, m.p. 318 - 320 °C; yield 6.25 g. (Found: C, 64.3; H, 3.6; N, 11.3. $C_{26}H_{18}N_4O_6$ requires C, 64.7; H, 3.8; N, 11.6%); $\nu_{max.}$ 1740 (CO), 1600, 1195, 960 cm^{-1}; ^1H n.m.r. not available because of low solubility; *m/z* (M^+ absent), 349 (v. weak), 258, 256, 224, 192.

2.3.6 Formation of 2,5-Ditolyl-1,3,4-thiadiazoles

2,5-Di-*p*-tolyl-1,3,4-thiadiazole. 1,2-Di-*p*-toluoylhydrazine (30.0 g, 0.111 mol.) and phosphorus pentasulphide (30.0 g, 0.135 mol.) were heated under reflux in xylene (250 ml) for 2 h. After cooling, water (150 ml) was added and the mixture was left to stand, with stirring, for 12 h. The solid collected by filtration, was extracted with ether (3 x 100 ml). The ether solution was washed with 1 M NaOH (3 x 10 ml), then water (1 x 25 ml) and dried ($MgSO_4$). A solid, obtained on removal of the solvent, formed small, white needles from ethanol. The ether-insoluble fraction of the solid was extracted with boiling DMF (250 ml). This on addition to water yielded a second crop, which was recrystallised as before; m.p. 158 °C (lit.[125] 156 - 158 °C); yield 19.8 g (66%).

2.3.7 The Oxidation of the Ditolyl-oxadiazoles and -thiadiazoles

(1,3,4-Oxadiazole-2,5-diyl)-4,4'-dibenzoic acid. Di-*p*-tolyl--1,3,4-oxadiazole (10 g, 0.04 mol.) was heated to 70 °C in a pyridine/water azeotrope (168 ml pyridine/108 ml water), whereupon potassium permanganate (40 g) was added in batches, over a period of 30 min. with stirring. The mixture was then heated under reflux for 2 h, after which time the solvents were removed at reduced pressure to leave a dark-brown residue which was washed with water (5 x 100 ml). After filtration, the filtrate on acidification, with dilute hydrochloric acid, gave the product as a gelatinous solution,

which was centrifuged, filtered, washed with water (100 ml) and dried at 100 °C. Due to the product's high insolubility, it was not recrystallised. M.p. 425 °C (lit.[103] 450 °C); yield 10.3 g (83%).

(1,3,4-Oxadiazole-2,5-diyl)-3,3'-dibenzoic acid was similarly prepared from 2,5-di-*m*-tolyl-1,3,4-oxadiazole (10.0 g, 0.04 mol.) and potassium permanganate (50 g); m.p. 368 °C (lit.[103] 368 - 371 °C); yield 9.5 g (77%).

(1,3,4-Thiadiazole-2,5-diyl)-4,4'-dibenzoic acid was prepared from 2,5-di-*p*-tolyl-1,3,4-thiadiazole (10.0 g, 0.038 mol.) and potassium permanganate (40 g); m.p. 425 °C (lit.[103] 450 °C); yield 10.0 g (81%).

2.3.8 Synthesis of 2,5-bis(p-acetoxyphenyl)-1,3,4-thiadiazole

Carboxymethyl *p*-hydroxydithiobenzoate was prepared by adding ammonium sulphide (135 ml) in 10 ml aliquots, over a period of 30 min, to a solution of *p*-hydroxybenzaldehyde (30.5 g, 0.25 mol.) in ethanol (90 ml) at 65 °C. The mixture was then heated for 10 min at reflux, immediately cooled in ice and acidified (conc. HCl). The red oil that formed was extracted with ether (3 x 150 ml) and this in turn extracted with 1 M sodium hydroxide (3 x 100 ml). An aqueous solution of chloroacetic acid (23.8 g, 0.25 mol.) preneutralised with solid sodium carbonate was added and the pH of the solution adjusted to 7. Solid began to precipitate from solution; on acidification (dil. HCl) more precipitate collected. Recrystallisation from water gave red needles, m.p. 192 °C (lit.[111] 194 - 197 °C); yield 4.7 g (7%). Carboxymethyl

p-hydroxydithiobenzoate (2.28 g, 0.01 mol.) was dissolved in 1 M sodium hydroxide (10 ml) and water (10 ml). The solution was cooled in ice and hydrazine monohydrate (0.5 g, 0.01 mol.) added. After 3 min the product had appeared and the solution had completely lost its red colour. Recrystallisation from ethanol/water (80/20) gave the product, *p*-hydroxythiobenzhydrazide, as white prisms, m.p. 198 °C (lit.[111] 200 - 201 °C); yield 1.1 g (66%). Carboxymethyl *p*-hydroxydithiobenzoate (2.28 g, 0.01 mol.) was dissolved in 1 M sodium hydroxide (10 ml), and to this was added *p*-hydroxythiobenzhydrazide (1.68 g, 0.1 mol.) in ethanol (5 ml). After 72 h the thiadiazole had crystallised out of solution. The crude product was acetylated (Section 2.3.1) and recrystallised from acetone as fine, white needles, m.p. 241 - 3 °C; yield 0.92 g (26%).

2.3.9 The Preparation of *p*-Acetoxyphenyl 6-Acetoxy-2-naphthoate

p-Hydroxyphenyl 6-acetoxy-2-naphthoate was prepared by the addition of 6-acetoxy-2-naphthoyl chloride (24.85 g, 0.1 mol.) in portions to a well-stirred solution of quinol (11.0 g, 0.1 mol.) in pyridine (50 ml). Stirring was continued for 4 h and the slurry was then added to water (250 ml) whereupon the product precipitated. Recrystallisation from DMF gave small, white needles, m.p. 204 - 206 °C; yield 17.7 g (55%). (Found: C, 70.5; H, 4.2. $C_{19}H_{14}O_5$ requires C, 70.8; H, 4.4%). The product was then acetylated (Section 2.3.1) to give *p*-acetoxyphenyl 6-acetoxy-2-naphthoate. Recrystallisation from acetic acid gave white prisms, m.p.

154 °C; yield 18.1 g (95%). (Found: C, 69.1; H, 4.4. $C_{21}H_{16}O_6$ requires C, 69.2; H, 4.4%.) $\nu_{max.}$ 1755, 1730, 1715, 1630, 1500, 1370, 1280 cm^{-1}; $\delta_H(CDCl_3)$ 2.53 (6H, s, CH_3), 7.25 - 8.50 (10H, m, Ar-H); *m/z* 364 (M^{+}), 322, 230, 213, 188, 171, 143.

CHAPTER 3

POLYMERS

3.1 NOMENCLATURE OF POLYMERS AND MONOMERS

A series of 51 copolyesters was produced, using various combinations and proportions of monomers. The monomers were divided into three categories: diacetates (AA type); dicarboxylic acids (BB type) and acetoxyl/carboxylic acids (AB type). To maintain a stoichiometric balance, the molar proportions of AA and BB type monomers have to be equal. As a result of the large number of monomers used, no simple system of nomenclature could be devised for the polymers, which would indicate the proportions of constitutent monomers. It was thus decided simply to number the polymers chronologically, indicating the ratio of constituent monomers by the use of brackets and subscripts. For example:

$$PX \; ; \quad (\alpha)_1 \quad (\beta)_1 \quad (\gamma)_2$$

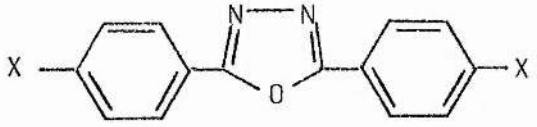
indicates that polymer, number X, is formed from one molar equivalent of both monomers α and β, and two molar equivalents of monomer γ. In this system of nomenclature, AA type monomers are stated first, *i.e.* in bracket α, BB type monomers secondly, (bracket β), and AB type monomers lastly, (bracket γ). There can of course be more than one monomer of each type.

The I.U.P.A.C. nomenclature for the monomers is prohibitively long for frequent use, and thus a system of abbreviations was devised, which helped to facilitate the use of the polymer nomenclature system. For simple monomers, *i.e.* those based on benzene or naphthalene, the code name adopted is generally derived from the systematic name of

the monomer.

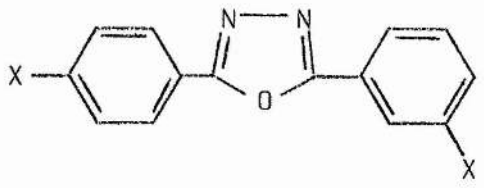
p-Acetoxybenzoic acid	pABA
m-Acetoxybenzoic acid	mABA
6-Acetoxy-2-naphthoic acid	ANA
Terephthalic acid	TA
Isophthalic acid	IA
Hydroquinone diacetate	HQA
2,7-Diacetoxynaphthalene	27N
1,5-Diacetoxynaphthalene	15N

The more complex monomers - those based on 2,5-diphenyl--1,3,4-oxadiazole, or the thiadiazole analogue - have an O to represent an oxadiazole ring, or an S to represent a thiadiazole ring. The positions of substituents on the phenyl units is denoted by P (*p*-acetoxyphenyl) and M (*m*-acetoxyphenyl). If the oxadiazole is symmetrical, the letter D is used to represent the prefix di-. Therefore, DPO has the structure:



i.e. both substituents para

whereas MPO, has the structure:



i.e. one substituent para, the other meta

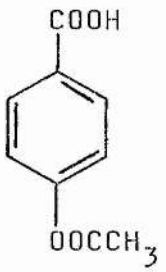
The corresponding dicarboxylic acids based on the diphenyl-oxadiazole structure are designated as for the

diacetates, but with a terminal A to signify the acid grouping; thus the two structures above in which X = COOH would be designated DPOA and MPOA respectively.

The monomers which contain more than one oxadiazole ring have these rings named separately. The term (OO) represents two oxadiazole rings joined directly, whereas (OPO) represents two oxadiazole rings joined by a *p*-phenylene unit, similarly (OMO) represents two oxadiazole rings joined by an *m*-phenylene unit. As previously, P is used to represent the position of the functional groups on the terminal phenyl groups.

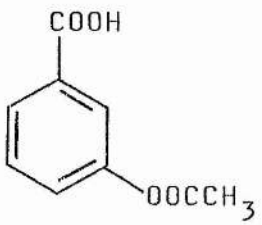
Figure 25 lists all the monomers used in the project, with their systematic names and their code names.

Figure 25



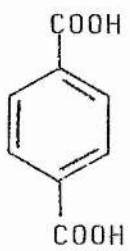
p-Acetoxybenzoic acid

pABA



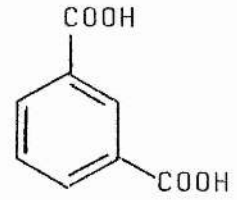
m-Acetoxybenzoic acid

mABA



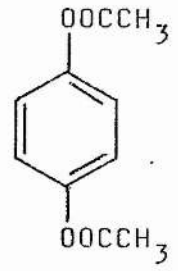
Terephthalic acid

TA



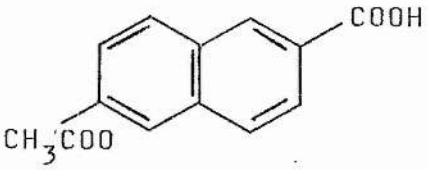
Isophthalic acid

1A



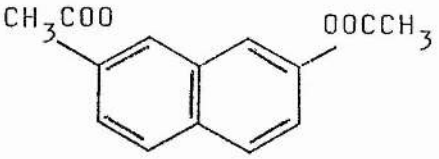
Hydroquinone diacetate

HQA



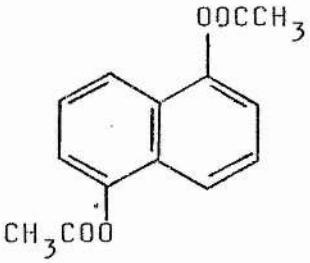
6-Acetoxy-2-naphthoic acid

ANA



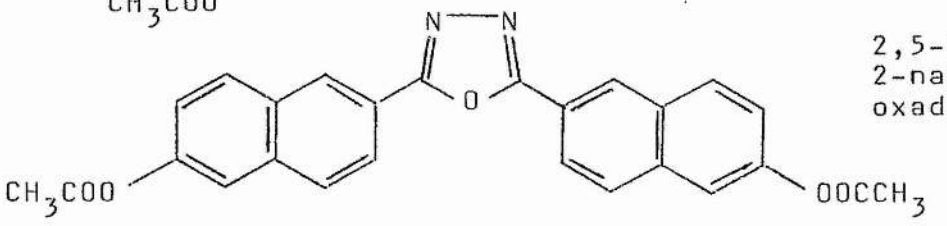
2,7-Diacetoxynaphthalene

27N



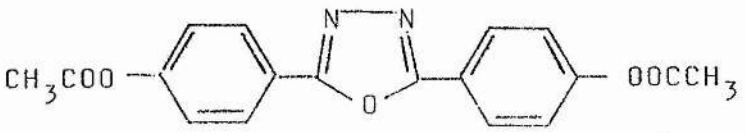
1,5-Diacetoxynaphthalene

15N



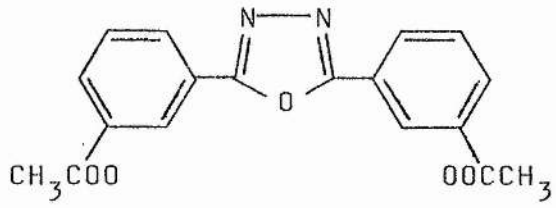
2,5-Bis(6-acetoxy-2-naphthyl)-1,3,4-oxadiazole

DNO

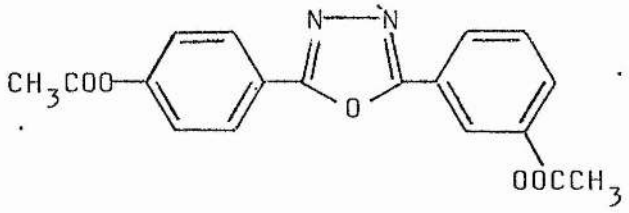


2,5-Bis(*p*-acetoxy phenyl)-1,3,4-oxadiazole

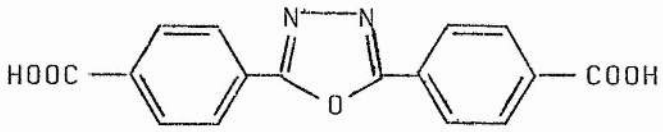
DPO



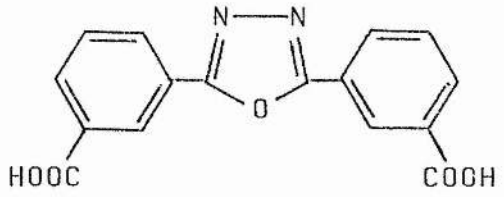
2,5-Bis(*m*-acetoxyphenyl)-1,3,4-oxadiazole, DMO



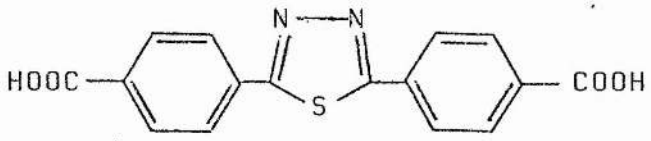
2-(*m*-Acetoxyphenyl)-5-(*p*-acetoxyphenyl)-1,3,4-oxadiazole, MPO



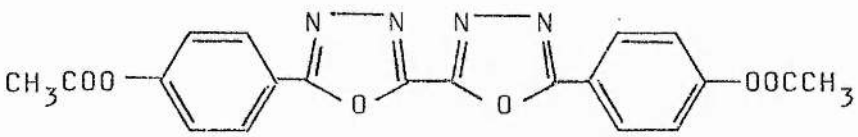
(1,3,4-Oxadiazole-2,5-diyl)-4,4'-dibenzoic acid, DPOA



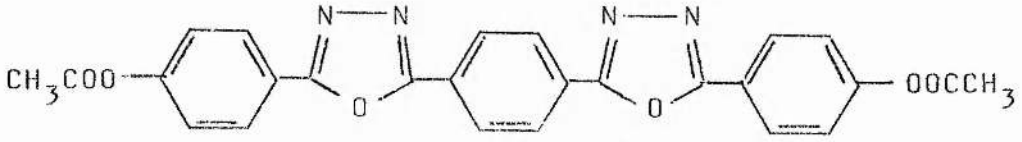
(1,3,4-Oxadiazole-2,5-diyl)-3,3'-dibenzoic acid, DMOA



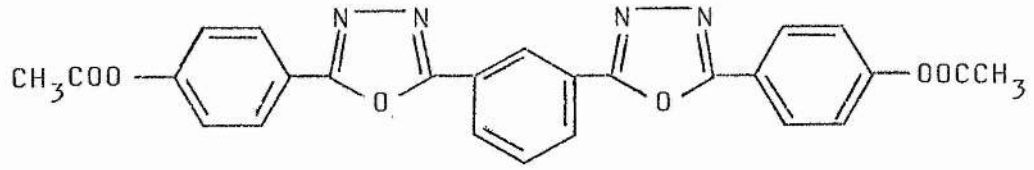
(1,3,4-Thiadiazole-2,5-diyl)-4,4'-dibenzoic acid, DPSA



2,2'-Bis[5-(*p*-acetoxyphenyl)-1,3,4-oxadiazolyl], DP(OO)



1,4-Bis[5-(*p*-acetoxyphenyl)-1,3,4-oxadiazol-2-yl]benzene, DP(OPO)



1,2-Bis[5-(*p*-acetoxyphenyl)-1,3,4-oxadiazol-2-yl]benzene, DP(OMO)

3.2 PRELIMINARY POLYMERISATION EXPERIMENTS

3.2.1 Preparation of the I.C.I. Standard Polymer Po

This polymer was suggested by I.C.I. to serve as a standard, with which comparisons could be made. The polymer has the composition:

$$Po \quad (HQA)_1 \ (TA)_1 \ (ANA)_2$$

The majority of the remaining 50 polymers have compositions based closely on this format.

Description of the Apparatus

The apparatus consisted of two components, the reaction flask, a Quickfit 100 ml long-neck, round-bottom flask and a specially prepared stillhead. The latter had two inlets above the reaction flask; one a screw adaptor to permit the entry of a stirrer, and the other connected to a nitrogen supply; a built-in condenser, which led to two other apertures, one for the collection of by-products, the other connected *via* cold traps to a vacuum pump. The pressure of the system was measured by a vacustat connected in parallel to the vacuum line. The paddle-shaped stainless steel stirrer bar was driven by a high torque stirrer and was sealed in the system by the screw-cap adaptor and two PTFE washers. This was found to provide adequate protection against possible leaks,

permitting the attainment of very low pressures.

The reaction flask was heated using a silicone oil bath and electric hot-plate.

Polymer Preparation

The reaction flask was charged with HQA (0.025 mol.), TA (0.025 mol.) and ANA (0.05 mol.). The apparatus was purged with nitrogen for 5 min, and was maintained under a constant flow of nitrogen, during the initial stage of the polymerisation. The temperature was raised at 10 °C/min up to a predetermined final temperature of 320 °C. At 180 °C the HQA melted, followed by the ANA at 210 °C; the TA slowly dissolved into solution, giving a dark brown liquid. At 250 °C, acetic acid began to distil, and by 285 °C the distillation was proceeding vigorously. A small amount of white crystals appeared on the cooler parts of the stillhead, although the majority of this was washed down into the reaction flask by the acetic acid. It was thought that the crystals were HQA, since this was the most volatile monomer, and it was feared that the stoichiometric imbalance that would result might produce a polymer of reduced strength.

As the acetic acid was collected, the reaction mixture slowly turned turbid, and after a further five minutes became a thin, cream-coloured, opaque melt. The viscosity of the melt increased as the quantity of acetic acid distillate increased. When the maximum temperature, 320 °C was reached, it was maintained for fifteen minutes, to ensure that all the by-product had been collected. The temperature was then allowed to drop to 260 °C, the nitrogen flow was stopped and

a vacuum applied gradually, to prevent the polymer rising and smearing on the reaction flask. A pressure of approximately 0.1 mmHg was maintained during the second stage of the polymerisation. The temperature was raised to 320 °C quickly, and the melt was stirred for a further 30 min. After this period, the polymer was allowed to cool quite rapidly in air.

The resulting polymer was smooth in texture and light cream in colour. It was moderately tough.

The HQA that had been deposited on the stillhead was identified from its infra-red spectrum, and was found to correspond to 2% of the total amount of HQA added. Thus a stoichiometric balance was indeed occurring and amendments to the procedure were sought in order to overcome this problem. Three modifications were tried:-

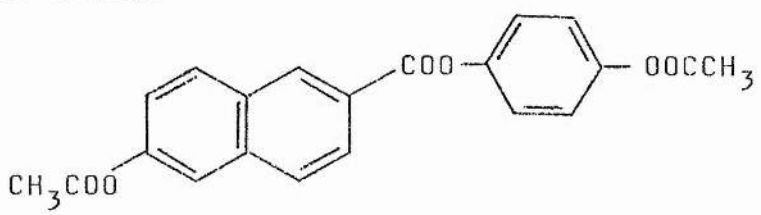
i) Pre-reaction of the HQA, to reduce its volatility.

ii) Use of a slurry polymerisation technique.

iii) Addition of a 2% excess of HQA.

i) *Pre-reacted HQA*

To prevent the loss of HQA by evaporation, the HQA was incorporated into the mixture as ANA-HQ, which has the structure below.



The overall composition of the polyer is the same as that previously made, but it has a different monomeric

make-up.

$$Po(A) \quad (ANA\text{-}HQA)_1 \ (TA)_1 \ (ANA)_1$$

The polymerisation procedure was the same as that previously used. However, a white solid deposit once again collected on the cooler regions of the condenser and this was again found to be HQA. It was believed that the HQA was being displaced from the ANA-HQA by transesterification with free ANA or acetic acid (or by a more complicated sequence).

Thus the loss of HQA was not prevented by this method and since extra stages were necessary in the monomer preparation, it was not employed further.

ii) *Slurry Polymerisation*

Using the same molar quantities of monomers as used in the first trial, acetic acid (20 mls) was added to produce a slurry. Both HQA and ANA are soluble in acetic acid, whereas TA is only sparingly soluble.

It was hoped that it would be possible to react the monomers in solution, thus reducing the volatility of the HQA and that the additional volume of by-product might help "wash" any HQA deposits back into the reaction flask.

The polymerisation was carried out exactly as before and this time no significant deposits of HQA could be seen. However, when the acetic acid was analysed, it was found to contain HQA; almost 4% of the original quantity of HQA added. It thus appeared that the acetic acid was augmenting the loss of HQA perhaps by co-distillation, and so this method was also abandoned.

iii) *Addition of Excess HQA*

Since 2% of the HQA added in the first polymerisation trial was lost by evaporation, it was decided simply to add a 2% excess of the monomer, to compensate for that lost during the process. Using exactly the same technique, the polymer obtained was very similar to that obtained from the first trial. Once again the HQA was collected and estimated to be approximately 2% of the total HQA. The polymer thus had an improved stoichiometric balance and would thus, hopefully, produce fibres with superior mechanical properties.

In other polymer preparations that involved the use of HQA, a 2% excess of that monomer was added, though this is not indicated by the value of the molar proportions written as subscripts outside the brackets.

3.2.2 Preparation of P1, P2 and P3

In P1, P2 and P3, the HQA is totally replaced by DPO, DMO and MPO respectively. Thus these polymers have the following compositions.

P1 $(DPO)_1\ (TA)_1\ (ANA)_2$

P2 $(DMO)_1\ (TA)_1\ (ANA)_2$

P3 $(MPO)_1\ (TA)_1\ (ANA)_2$

During the preparation of these polymers, the stoichiometric balance was easily maintained, as the volatile HQA was replaced by involatile oxadiazole-containing species.

The polymers were prepared by the same method used to prepare Po. P1 was dark brown, smooth and tough. P2 and P3 were light brown in colour, smooth but less tough.

Initial tests carried out by the New Science Group of I.C.I. however, proved disappointing. The three polymers, although liquid crystalline, were found, by melt-flow index, to be of molecular weight too low to produce fibres of reasonable length. However, initial indications were that P1 had better properties than P2 and P3, and it was thus decided to make polymers based only on DPO.

X-ray diffraction studies, carried out by Dr. J. G. Tomka at the University of Leeds, also had a disappointing outcome. All these polymers showed only a broad halo (Figure 26); there were no rings indicating crystallinity or even para-crystallinity. It was thought quite possible that the chemical structures were so disrupted by the high proportion of angular segments, that the development of crystalline or paracrystalline order was wholly suppressed. It was decided

Figure 26

that the use of X-ray diffraction as an analytical method was

of little value at this stage and was not used in this work until fibres were produced.

It was still however necessary to increase the molecular weight of the polymers. Three techniques were tried:-

i) Using a higher end temperature, *i.e.* 340 °C.

ii) Using potassium acetate (50 p.p.m.) and acetic anhydride (2.4%) as a catalyst. This procedure was suggested by I.C.I. New Science Group.

iii) By increasing the duration of the final stage of polymerisation, *i.e.* maintaining the polymer at 320 °C until it can no longer be stirred.

P1 was then made using the standard method with each of these three modifications. The polymer obtained by using the first modification was a very dark brown and it was feared that degradation and/or side-reactions might have occurred. The polymer obtained using the second modification appeared no different from that obtained in the original preparation. The polymer from the third modification was, however, very much altered. It was only slightly darker in colour than the original polymer, but was exceedingly fibrous and very tough.

Modification (iii) was thus adopted for subsequent polymer preparations: the stirring of the polymer under vacuum at 320 °C was sustained until this became impracticable due to the viscosity of the melt, or until two hours had passed.

In several of the later polymerisations, especially those

of polymers based on DMOA and DPSA, the end temperature was lowered as these melts were believed to be isotropic at 320 °C. In other cases, on the application of the vacuum, the melt solidified and thus could not be processed further. In these instances end temperatures are not given.

Table 3 lists all polymers made in this work, and their compositions.

3.3 POLYMER CHARACTERISATION

3.3.1 General

A total characterisation of any polymeric material involves the study of its chemical and physical structures as well as determination of its properties. In this work, 51 copolyesters of different compositions were prepared and the characterisation techniques used were concerned with determining the correlations, if any, of the properties imparted to the polymers by the different compositions. Ideally the study of the chemical structure of polymers requires the determination of:

i) the constitution, configuration, proportion, and sequence of repeating units, and the overall conformation of the polymer chain,

ii) the type and proportion of end-groups,

iii) the molecular weight and molecular weight distribution.

In this work the constitution, configuration and proportion of repeating units are known, and although the sequence

Table 3

Polymer No.	Composition
0	$(HQA)_1\ (TA)_1\ (ANA)_2$
1	$(DPO)_1\ (TA)_1\ (ANA)_2$
2	$(DMO)_1\ (TA)_1\ (ANA)_2$
3	$(MPO)_1\ (TA)_1\ (ANA)_2$
4	$(DPO)_{\frac{3}{4}}\ (HQA)_{\frac{1}{4}}\ (TA)_1\ (ANA)_2$
5	$(DPO)_{\frac{1}{2}}\ (HQA)_{\frac{1}{2}}\ (TA)_1\ (ANA)_2$
6	$(DPO)_{\frac{1}{4}}\ (HQA)_{\frac{3}{4}}\ (TA)_1\ (ANA)_2$
7*	$(DPO)_1\ (TA)_1$
8	$(DPO)_1\ (DPOA)_1\ (ANA)_2$
9	$(DPO)_1\ (DPOA)_1\ (pABA)_2$
10	$(HQA)_1\ (DPOA)_{\frac{1}{2}}\ (TA)_{\frac{1}{2}}\ (ANA)_2$
11*	$(TA)_1\ (ANA)_2$
12	$(ANA\text{-}HQ)_1\ (TA)_1\ (ANA)_1$
13	$(DPO)_1\ (TA)_1\ (ANA)_1$
14	$(DPO)_1\ (TA)_1\ (ANA)_3$
15	$(DPO)_1\ (IA)_1\ (ANA)_2$
16	$(DPO)_1\ (TA)_1\ (pABA)_2$
17	$(DPO)_1\ (TA)_1\ (mABA)_2$
18	$(27N)_1\ (TA)_1\ (ANA)_2$
19	$(27N)_1\ (TA)_1\ (pABA)_2$

Table 3 (cont'd)

Polymer No.	Composition
20	$(27N)_1\ (TA)_1\ (mABA)_2$
21 †	$(27N)_1\ (IA)_1\ (ANA)_2$
22 †	$(27N)_1\ (IA)_1\ (pABA)_2$
23	$(DPO)_{\frac{1}{2}}\ (27N)_{\frac{1}{2}}\ (TA)_1\ (ANA)_2$
24	$(DPO)_{\frac{1}{2}}\ (27N)_{\frac{1}{2}}\ (IA)_1\ (ANA)_2$
25	$(15N)_1\ (TA)_1\ (ANA)_2$
26	$(15N)_1\ (TA)_1\ (pABA)_2$
27	$(15N)_1\ (TA)_1\ (mABA)_2$
28	$(15N)_1\ (IA)_1\ (ANA)_2$
29 †	$(15N)_1\ (IA)_1\ (pABA)_2$
30 †	$(DPO)_1\ (IA)_1\ (ANA)_1$
31	$(DPO)_1\ (IA)_1\ (ANA)_3$
32	$(DNO)_1\ (TA)_1\ (ANA)_2$
33	$(DNO)_1\ (TA)_1\ (pABA)_2$
34	$(DNO)_1\ (TA)_1\ (mABA)_2$
35 *	$(DNO)_1\ (IA)_1\ (ANA)_2$
36 *	$(DNO)_1\ (1A)_1\ (pABA)_2$
37 *	$(DNO)_1\ (TA)_1\ (ANA)_3$
38	$(DNO)_1\ (IA)_1\ (ANA)_3$
39	$(HQA)_1\ (DPOA)_{\frac{1}{2}}\ (IA)_{\frac{1}{2}}\ (ANA)_2$

Table 3 (cont'd)

Polymer No.	Composition
40	$(27N)_1\ (DPOA)_1\ (ANA)_2$
41	$(15N)_1\ (DPOA)_1\ (ANA)_2$
42 $^{\alpha}$	$(HQA)_1\ (DMOA)_1\ (ANA)_2$
43 $^{\beta}$	$(15N)_1\ (DMOA)_1\ (ANA)_2$
44 $^{\gamma}$	$(27N)_1\ (DMOA)_1\ (ANA)_2$
45 *	$(HQA)_1\ (DPSA)_1\ (ANA)_2$
46 $^{\gamma}$	$(15N)_1\ (DPSA)_1\ (ANA)_2$
47	$(27N)_1\ (DPSA)_1\ (ANA)_2$
48	$(DP(OO))_1\ (TA)_1\ (ANA)_2$
49 †	$(DP(OPO))_1\ (TA)_1\ (ANA)_2$
50 *	$(DP(OMO))_1\ (TA)_1\ (ANA)_2$

All end temperatures, unless indicated otherwise below, were 320 °C.

* - No end temperature recorded as polymer solidified on the application of the vacuum.

† - Stirring of the polymer was only possible for a short period of time (20 mins), after the application of the vacuum, as the polymer gradually solidified.

$^{\alpha}$ - End temperature of 300 °C

$^{\beta}$ - End temperature of 220 °C

$^{\gamma}$ - End temperature of 280 °C

is random, the overall conformation of the molecule is predictable by virtue of the rigidity of the monomer units.

The nature of the end-groups may obviously be either hydroxyl or carboxylic acid, but no attempt has been made to determine the proportion of each in any given sample.

It was not easy to obtain a measurement of the molecular weight or molecular weight distribution, because the polymers were so sparingly soluble in the vast majority of conventional solvents. In other works dealing with insoluble polymers, intrinsic viscosity has been used to obtain a relative measure of the molecular weight, but this is only applicable when all the polymers have the same fundamental composition and thus was not of real value in this work.

The physical properties which were most important in relation to this work, are the transition temperatures and the thermal stability of the polymers, since these determine the properties of the fibres. Above the glass transition temperature (Tg), an aromatic copolyester may melt and this may result in the formation of a nematic liquid (Tcn); at a higher temperature this nematic melt becomes an isotropic melt (Tni). In the case of conventional polymeric materials, *e.g.* PET, an isotropic melt is obtained directly from the solid (Tci). The methods used in this study to determine these values were hot-stage microscopy (HSM) and differential scanning calorimetry (DSC).

As with conventional polymers, the degree of order of a given material is strongly influenced by its complete thermochemical history. For proper comparisons to be made it is

necessary to pre-treat the polymers either by quenching or annealing, since in this way any thermochemical history differences may be minimised. However, when samples of various polymers in these series were annealed, their DSC thermograms revealed no changes. This is expected since the degree of ordering, even with annealing is minimal. An x-ray diffraction study on these annealed samples showed no signs of crystallinity or paracrystallinity, only the same broad halo as in the unannealed samples. (Figure 26). Thus all characterisations were carried out using the "as made" polymers.

Out of the 50 polymers prepared, 18 were chosen for full characterisation, on the basis of initial HSM observations, and these were compared with a conventional polymer (PET) as well as with the ICI polymer Po. For comparison purposes, the 18 polymers could be grouped according to their compositions:-

0,1,4,5,6	Progressive replacement of HQA in Po by DPO.
1,13,14	DPO-containing polymers, with varying amounts of ANA.
1,15,16,17	Polymers based on P1 compositional format with differing BB and AB monomers.
1,18,23,25 32,48	Polymers based on P1 compositional format with various AA monomers
41,43,46	Polymers containing oxadiazole and thiadiazole diacids.

3.3.2 Determination of Transition Temperatures

The transition temperatures, Tg, Tcn, Tni and Tci are best estimated using a combination of hot-stage microscopy (HSM) observations and differential scanning calorimetry (DSC). HSM was used to identify which polymers formed nematic mesophases, and at what temperature any transitions occurred. (The maximum temperature that could be attained by this method was 350 °C.) The heating rate was not constant throughout the range, and decreased with increasing temperature. (Table 4)

Table 4

Average heating rate (°C/min)	Temperature Range (°C)
50	20 - 200
20	200 - 280
15	280 - 300
8	300 - 325
5	325 - 350

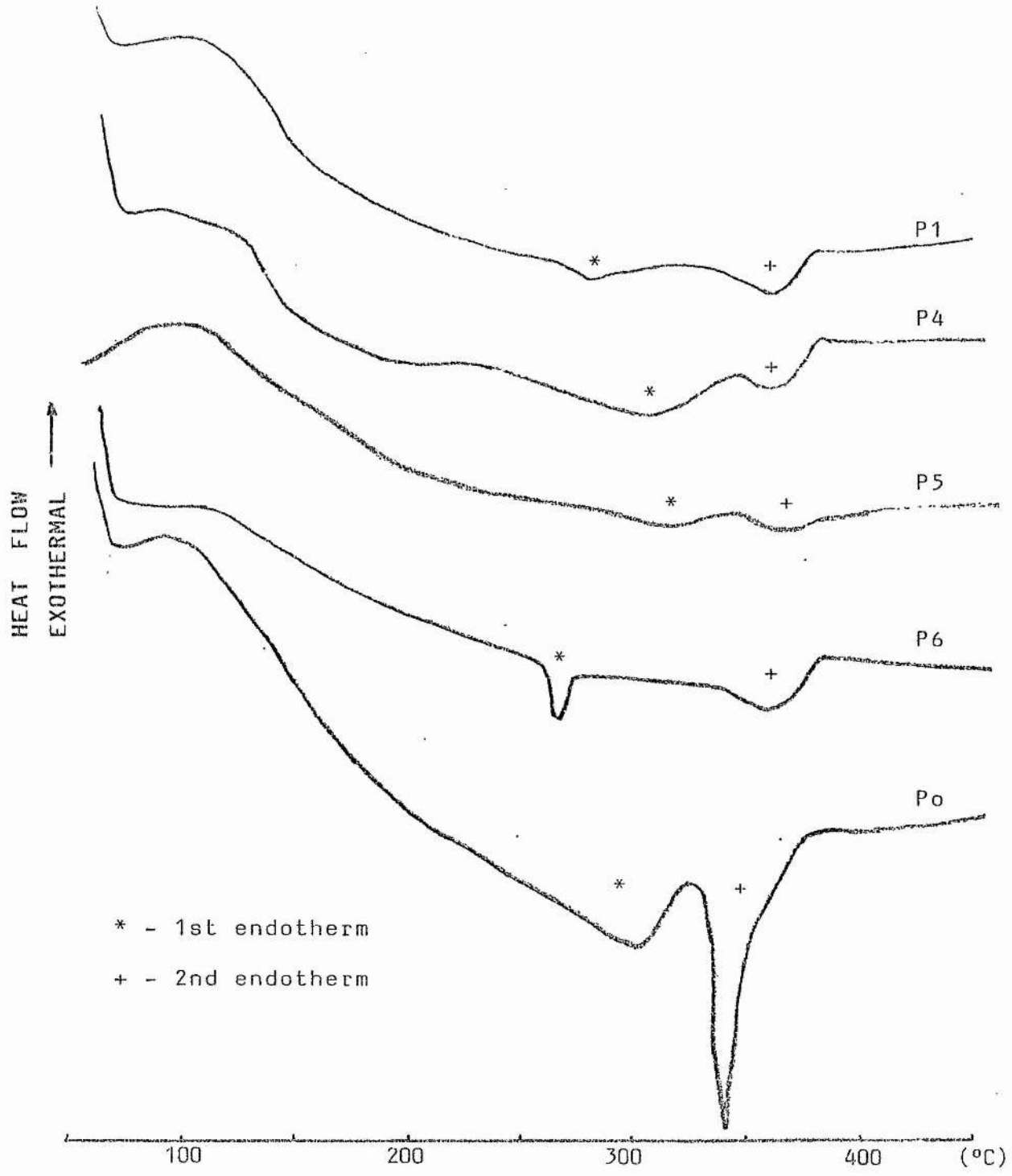
Tcn was taken to correspond to the onset of liquid-like mobility of the polymer, found by pressing the sample between the two microscope slides. The isotropisation temperature, Tni, was rarely recorded since these were generally greater than 350 °C and were thus outwith the range of observation.

DSC thermograms were obtained using a Mettler TC10 cell coupled to a Mettler TA 3000 processor. The calorimeter was calibrated using high purity metal standards (In, Zn and Pb). The samples were contained in sealed aluminium pans and

scanned from 50 - 590 °C at a rate of 50 °C/min under a flow of nitrogen. An empty pan and lid were used as the reference. Care was taken at all stages to keep the pan and lids free from contamination and mechanical damage as this increases the background noise and can create artefacts on the thermograms.

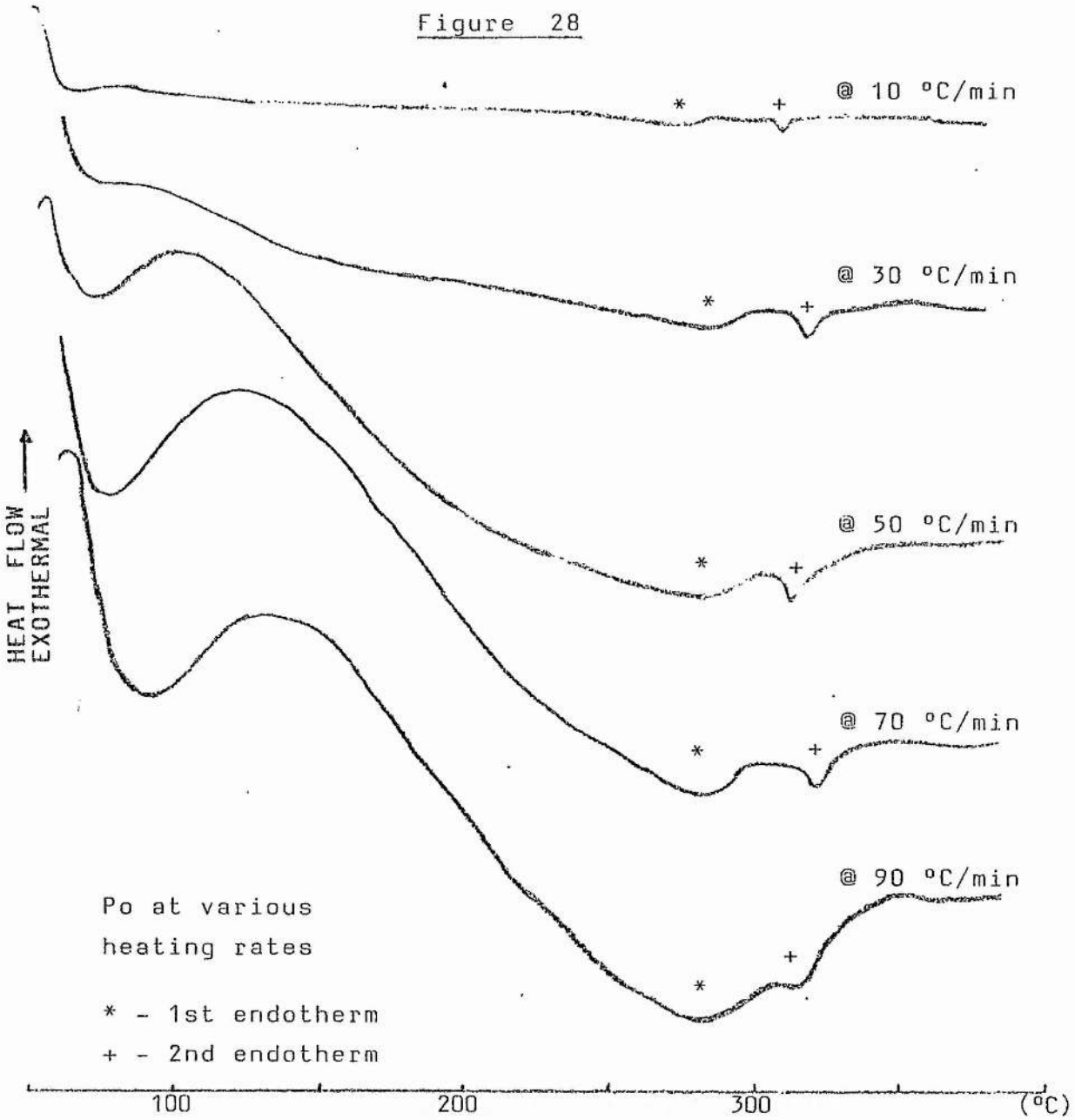
Figure 27 illustrates the DSC thermograms obtained for Po, P1, P4, P5 and P6. It is observed that they all apparently show double melting points, a phenomenon which has been previously observed by several other groups.[130-132] The highest endotherm on a thermogram is generally broad and corresponds to a transition from a liquid crystalline phase to an isotropic phase. Transitions from the solid to the nematic phase may be accompanied by one or more first--order transitions. Where multiple transitions occur, it is presumed that of the lower temperature DSC peaks, the solid-to-nematic transition corresponds to the peak of the highest transition temperature. An explanation of the multiple melting phenomenon is that it arises from a crystallisation of the polymer chains. This view is supported by the relative changes in size of the two endotherms as the DSC heating rate is altered. With increasing heating rate, the higher temperature endotherm becomes smaller, and the lower temperature endotherm becomes proportionally larger. The higher temperature endotherm apparently results from the melting of polymer crystals which were formed from the amorphous polymer by simultaneous melting and recrystallisation at lower temperatures. The melting endotherm and the recrystallisation

Figure 27



exotherm are thought to cancel each other thereby explaining the absence of a recrystallisation exotherm.[133] Since higher

Figure 28



heating rates allow for less recrystallisation, the relative magnitude of the higher temperature transition is diminished. This is shown in Figure 28, which illustrates thermograms of Po, at heating rates of 10, 30, 50, 70 and 90 °C/min. It should be noted that the two endotherms are separated by a large temperature difference (~60 °C). It was at first thought that the higher endotherm corresponded to the

nematic-to-isotropic transition, but the use of more sophisticated HSM at Leeds, using temperatures of up to 600 °C, showed that Po, P1, P4, P5 and P6 were all liquid crystalline up to temperatures of approximately 450 °C, when they then started to degrade. Thus the second endotherm is believed not to correspond to Tni, but to the melting of a more stable crystalline form. The lower endotherm is believed to represent the temperature at which a less stable crystalline form melts If the polymer did not crystallise at all, then only a gradual endothermic process would be observed as the amorphous material gradually softened resulting in only a sloping baseline on the thermogram.

Investigations of several literature polymers with well-defined double endotherms under a polarising microscope at temperatures between their endotherms showed no fluidity due to a transition of the less perfect crystal form to the nematic phase.[130-132] However, the partial melting of the sample still leaves the crystal structure of the more stable form intact, and it would not be expected that the sample as a whole would become fluid until both crystal forms had melted.

In the present work a comparison of the estimated endotherms (the end temperatures being taken) on the thermograms, with the temperatures obtained by HSM where fluidity of the polymers was first observed, are in disagreement. (Table 5).

In every case, fluidity was observed by HSM at temperatures well below those expected from the DSC results. It is suggested that, (apart from Po), duc to the angular segments the polymers were completely amorphous, and even at very

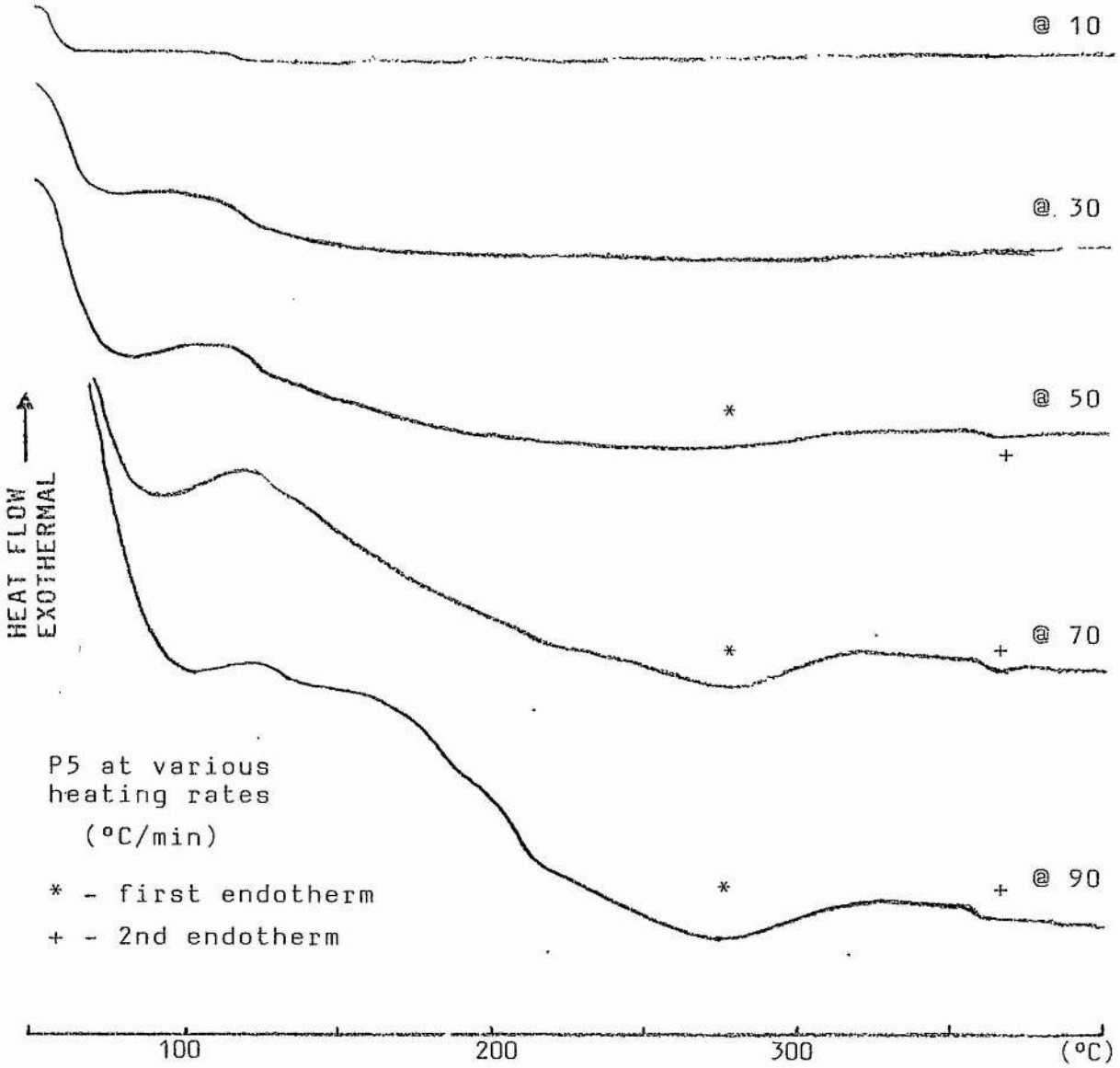
Table 5

	Low Endotherm (°C)	High Endotherm (°C)	HSM (°C)
Po	330	380	300
P1	300	380	270
P4	335	380	220
P5	-	380	220
P6	270	385	260

slow heating rates the degree of crystallisation that would be expected to occur is quite small. Thus these polymers remain almost purely amorphous, and on further heating behave like any other amorphous polymer; above Tg, a "rubbery state" is obtained, and with further heating a "rubbery flow" is obtained. It could thus be this "rubbery flow" which is being observed by HSM at temperatures below the first endotherm. This would also explain why at this stage the polymers are viscous, uniform, olive-green in colour, and display birefringence only at the edges (where they are thinnest), and why they gradually brighten to a silver-coloured, very bright, thin "melt", with a threaded texture, as the temperature approaches that of the first endotherm. (Photographs of the solid phase, the "rubber flow", the nematic and istropic phases, are displayed on pages 103 to 110, of some of the more interesting examples. The photographs were taken on 35 mm 400 ASA Kodacolour film through a camera attached directly to the viewing piece of the microscope.)

In the case of Po, since it contains no angular disrupting groups, it may undergo a recrystallisation at slower heating

Figure 29



rates and thus its DSC thermograms should be affected by heating rates, whereas those of the other polymers, which contain angular segments, should be less affected, since the amount of recrystallisation that occurs is small. The various thermograms of Po are already given in Figure 28, and the relationship of the two endotherms has been explained. The thermograms of P5 are given in Figure 29, and it should be

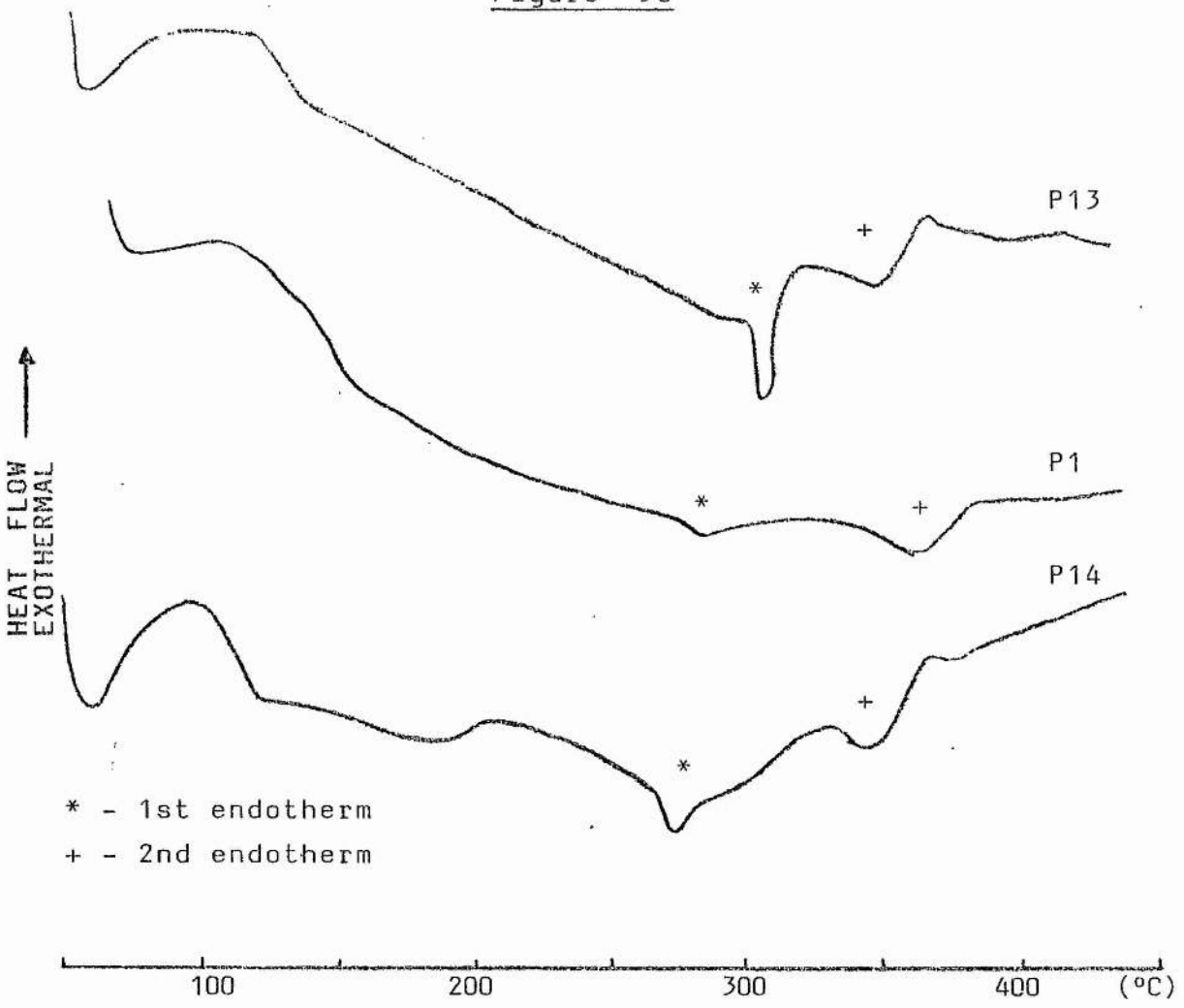
noted that although the thermograms differ in shape (as do those of Po) with increasing heating rate, the second endotherm is of less significance than that seen in Po, and is consistent with the degree of crystallisation that one would expect to occur. The thermograms of P5 are overall less characteristic.

If a polymer contains a large proportion of angular segments, such as DPO, 27N or DNO, *etc.*, the first endotherm represents the most important transition since the amount of crystallisation to the more stable form is small, and this temperature gives an indication of the point at which the sample can be thought of as nematic liquid. It is believed that at this point any remaining crystallites can be envisaged as being in a solution. This temperature is denoted by Tcn(1), whereas the second endotherm is termed Tcn(2).

Figure 30 shows the thermograms of P1, P13 and P14. The most noticeable feature is, once again, the double melting points. With increasing the proportion of ANA, there is a corresponding drop in Tcn(1).

Figure 31 shows the thermograms of P1, P15, P16 and P17. In this series of polymers, the AA-type monomer is always DPO, but the BB-type and AB-type monomers vary. The proportion of AA : BB : AB is however always 1 : 1 : 2. By replacing the TA in P1, with IA, Tcn(1) is lowered from ~300 to ~250 °C. This is expected when the proportion of angular disruptors is increased. Replacing the ANA in P1, with pABA results in an increase in Tcn(1), and when the ANA

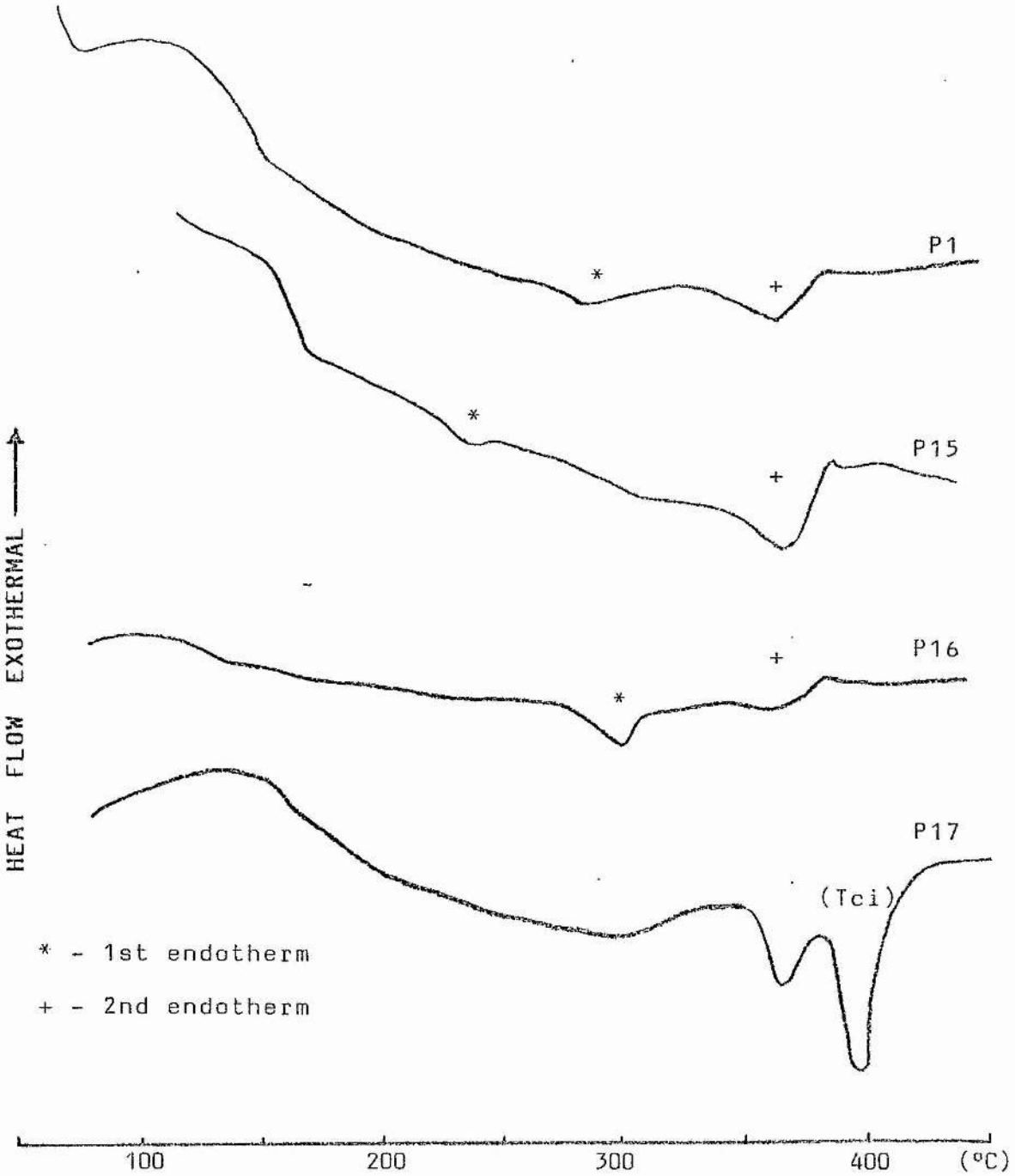
Figure 30



is replaced by mABA (increasing the non-mesogenic content to 75%), the resulting polymer is not liquid crystalline.

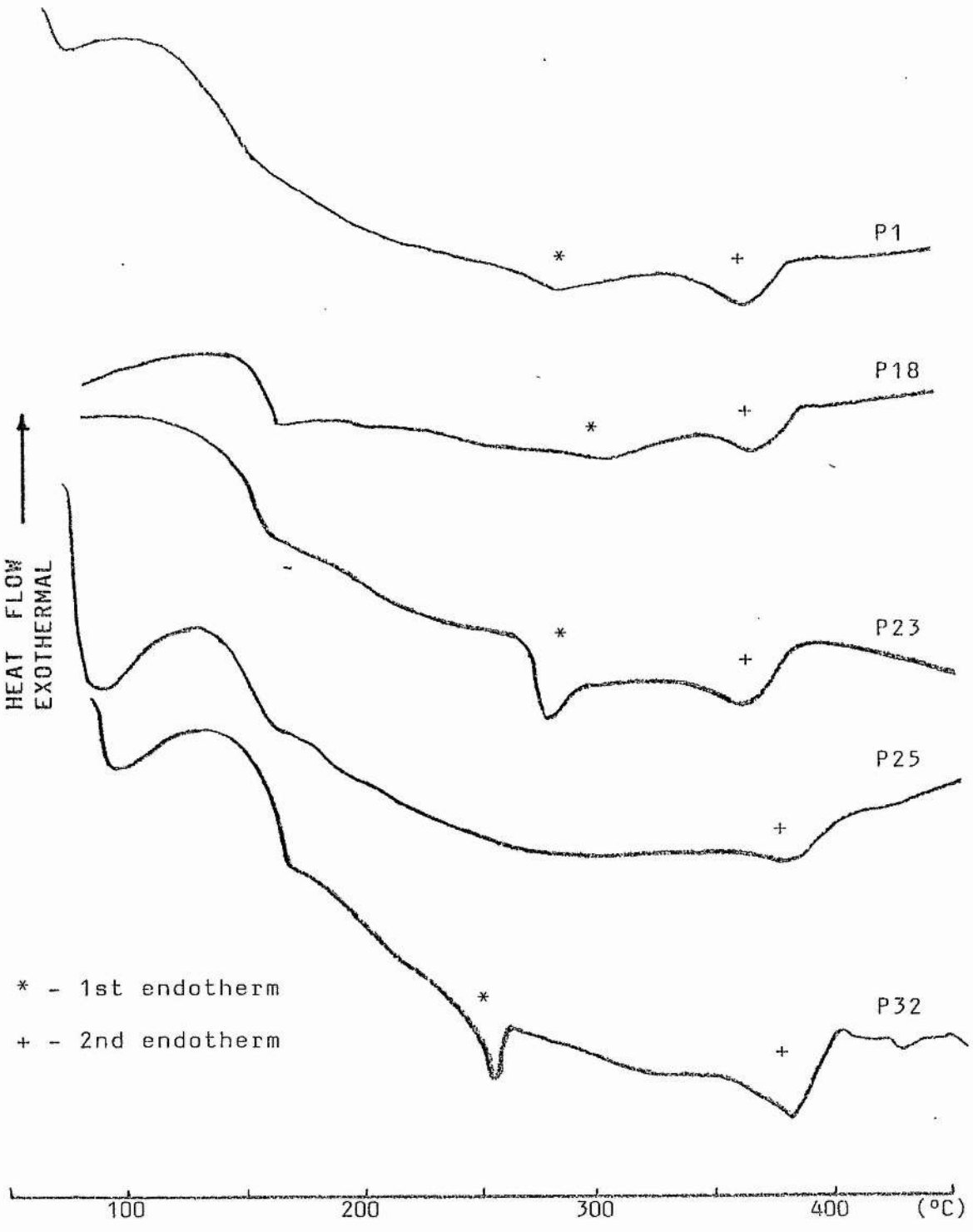
Figure 32 shows the thermograms of P1, P18, P23, P25 and P32. With this series of polymers only the AA-type monomers are changed. Replacement of DPO in P1 with 27N, causes a slight increase in Tcn(1). Replacement of half of the DPO with 27N, however, depresses the value of Tcn(1). This reduction is probably due to the increased randomisation within the polymer chains. Replacement of the DPO by 15N, which is mesogenic, should create a small increase in the

Figure 31



value of Tcn(1); however the endotherm is not observed. Replacement of DPO with DNO causes a considerable lowering in the value of Tcn(1). This is most likely due to the fact

Figure 32



that DNO is more disruptive, having both angular and lateral disruptive effects.

Figure 33

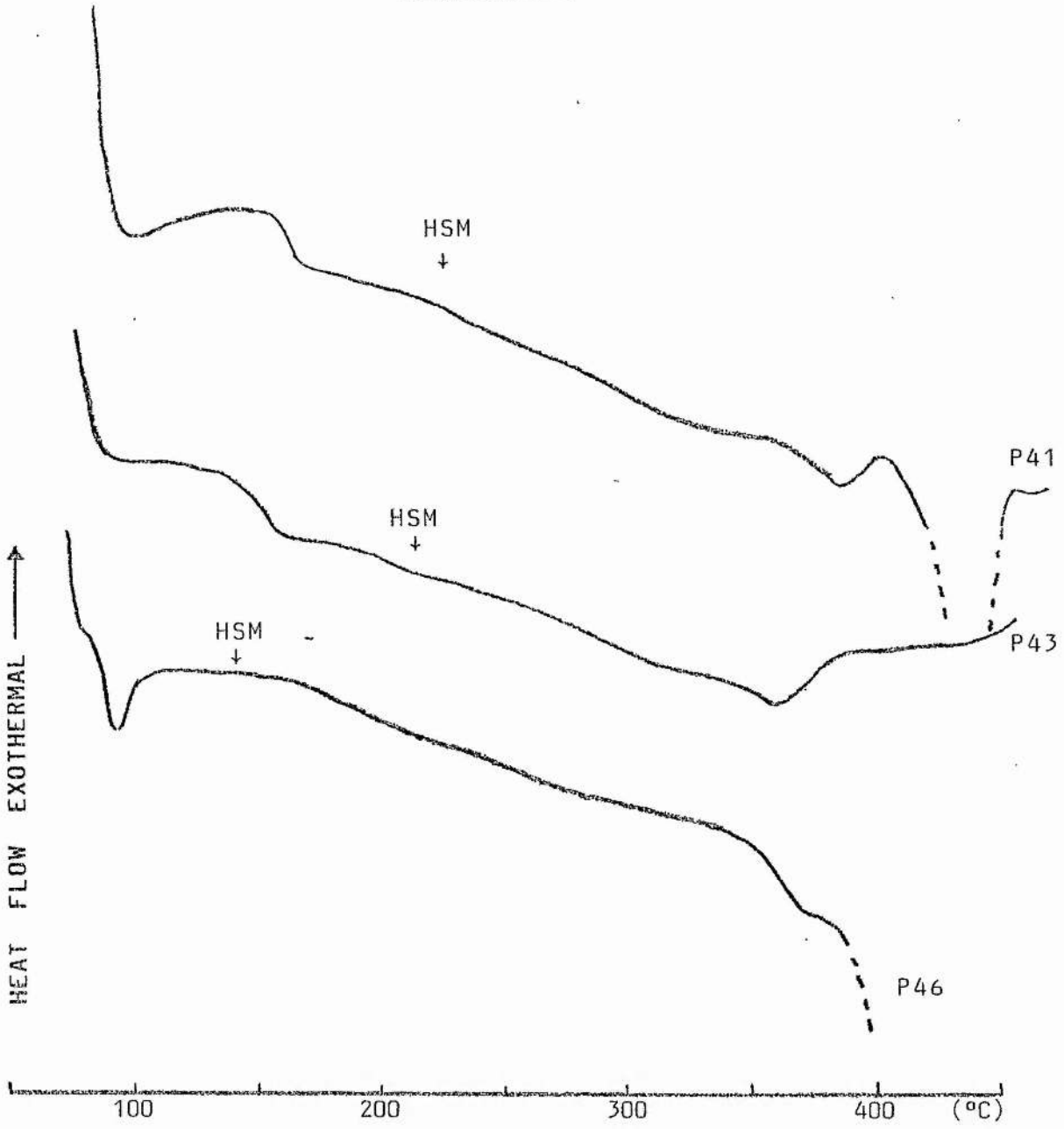
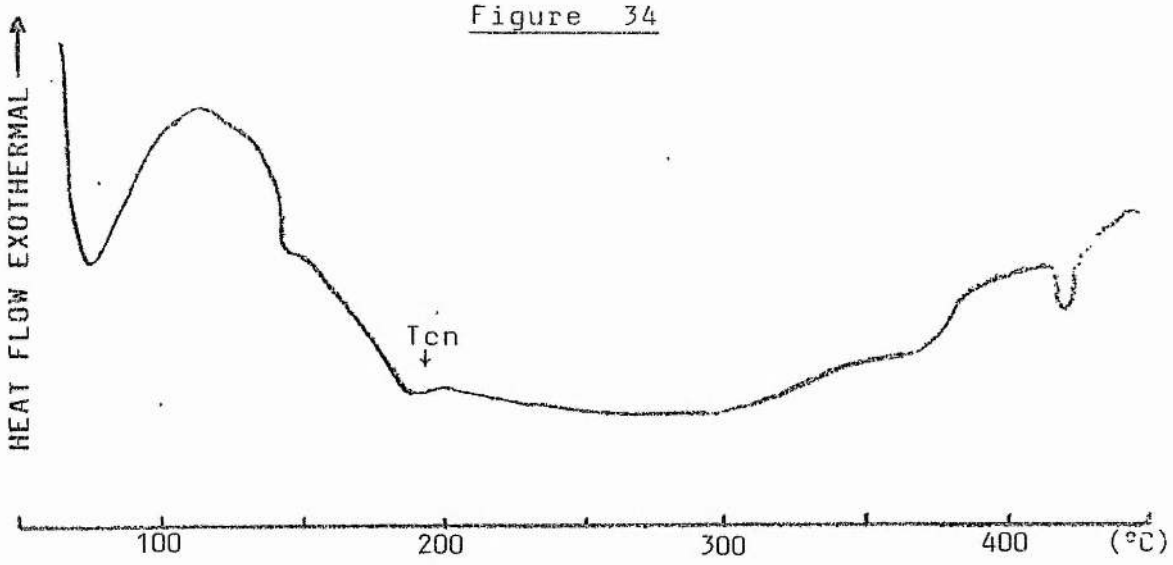


Figure 33 illustrates the thermograms of P41, P43 and P46, which contain the monomers DPOA, DMOA and DPSA respectively. Unlike the previous polymers, these polymers have low solid-to-nematic transition temperatures as observed by HSM, and these transitions are accompanied by quite sudden and rapid flowing. The DSC thermograms of these polymers are not

Figure 34



as informative as those of the other polymers but there appears to be no obvious double melting point phenomenon. It is possible that these polymers may be partly crystalline (although no X-ray data have to date been obtained). The thermograms of the three polymers do not reveal much information. The temperatures at which flow occurred (by HSM) is marked on each thermogram. The large endotherms at *ca.* 400 °C on the thermograms of P41 and P46 are due to degradation.

The thermogram of P48 shows an endotherm at 200 °C, which corresponds well with the temperature of 190 °C found by HSM. It can also be noted that the replacement of DPO in P1, by DP(OO) brings about a marked drop in temperature of the solid--to-nematic phase transition (Figure 34). The reason for this drop in Tcn(1) is most probably due to the lateral disruption created by the monomer DP(OO). (Chapter 2, page 50).

3.3.3. Photography

The following plates show the different phases one observes using a polarising microscope. The magnification used for all

plates was X40. The threaded texture, very common in thermotropic nematic melts, is not always apparent in the plates.

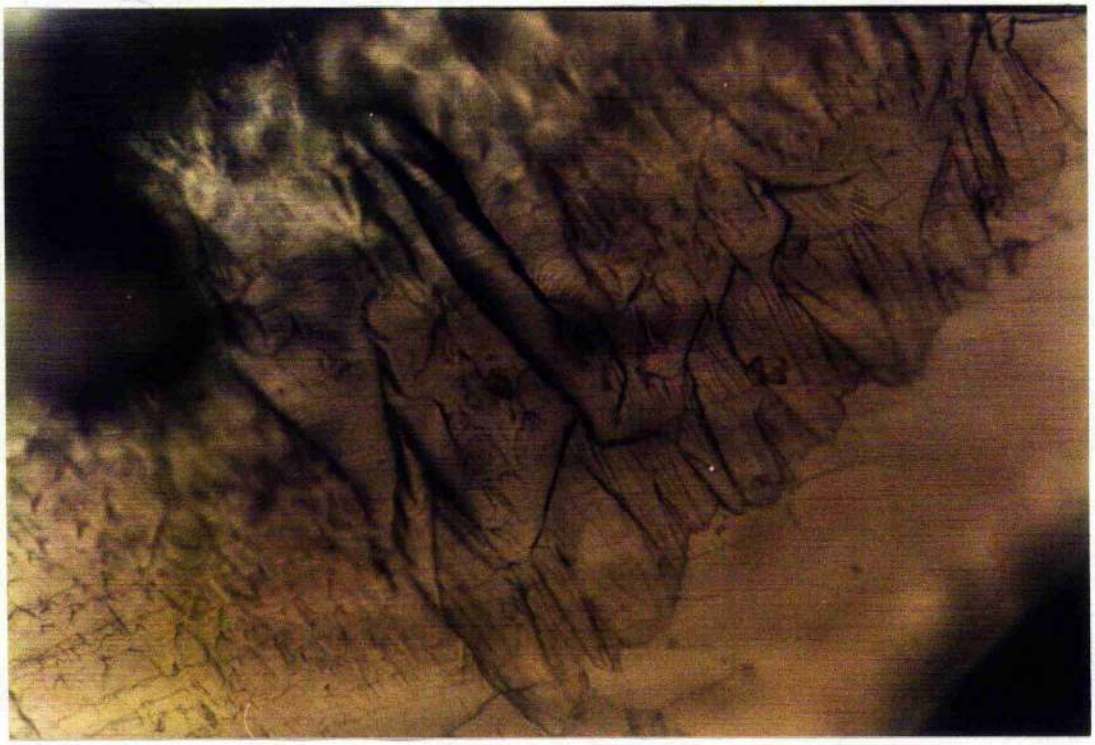


Plate 1 - this shows a thin slice of PET at 50 °C. The solid is light-transmitting; this is indicative of some ordering within the sold (*cf.* bottom right corner - dark background).

Plate 2 - this shows the isotropic melt of the PET. It is noted that the liquid is not light-transmitting, since there is no ordering in isotropic melts.

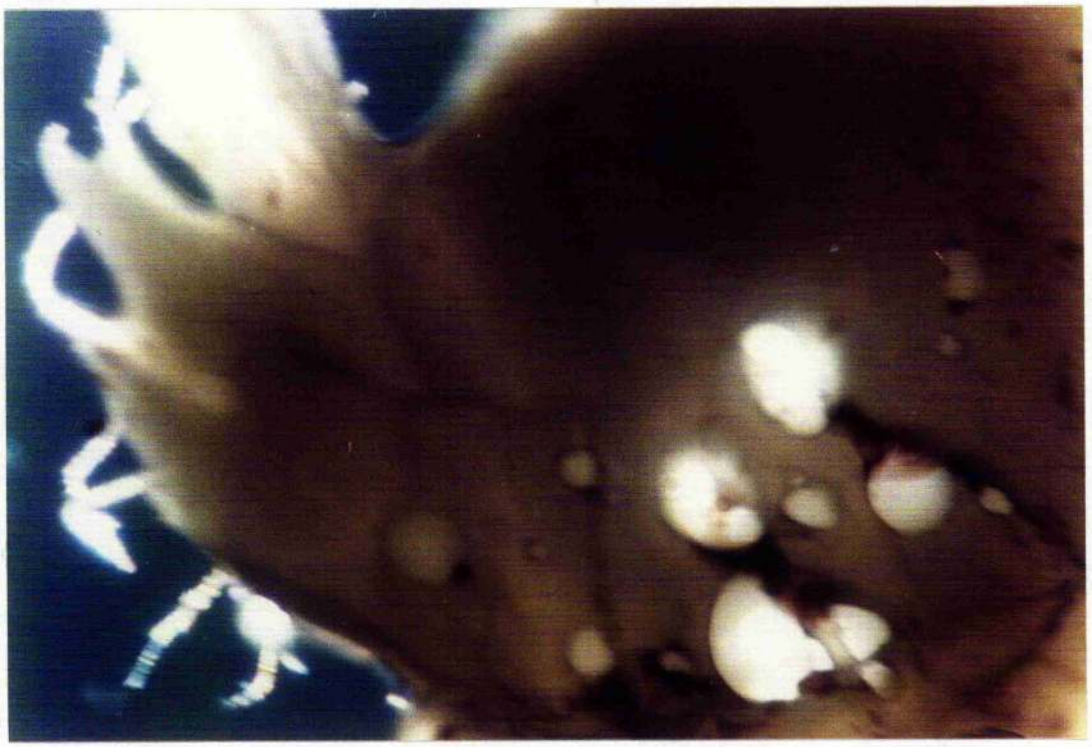


Plate 3 - this is the "rubber melt" formed by heating P1 to *ca.* 250 °C. At this stage, the melt is very viscous and does not shear easily. With increasing temperature, the "rubber melt" changes to a silver, fluid melt, which is nematic.

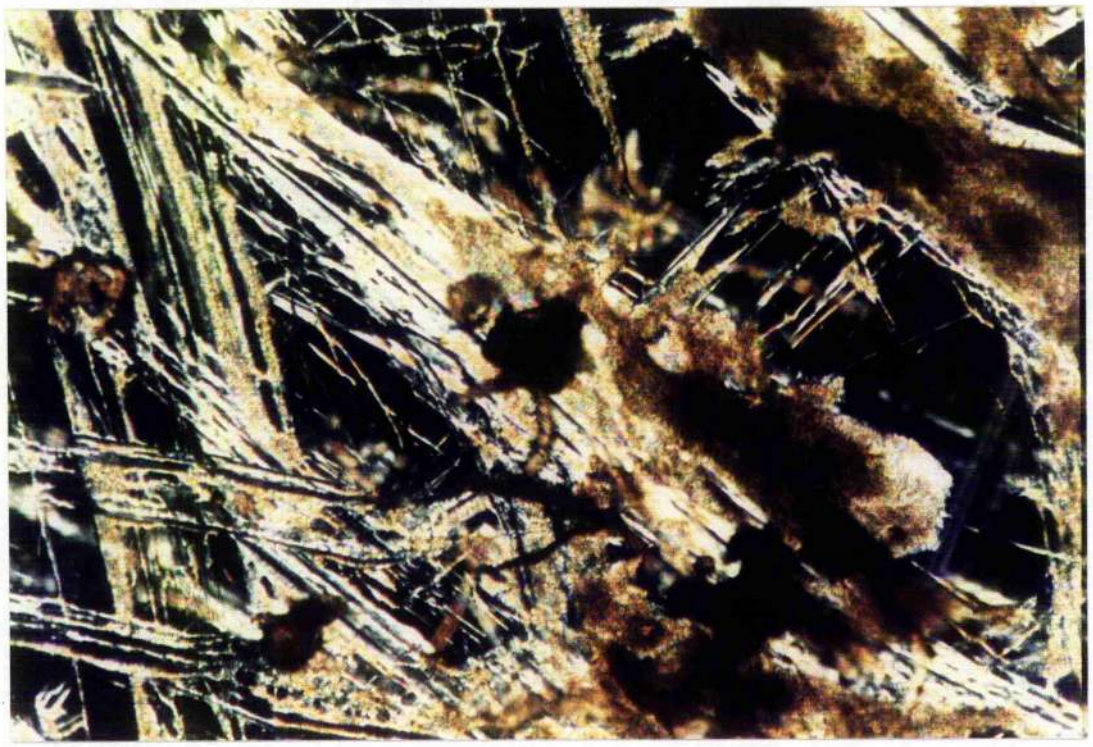


Plate 4 - the effect of shearing P1 at 250 °C

Plate 5 - the amorphous solid P13 (*cf.* with the partly crystalline PET, plate 1).

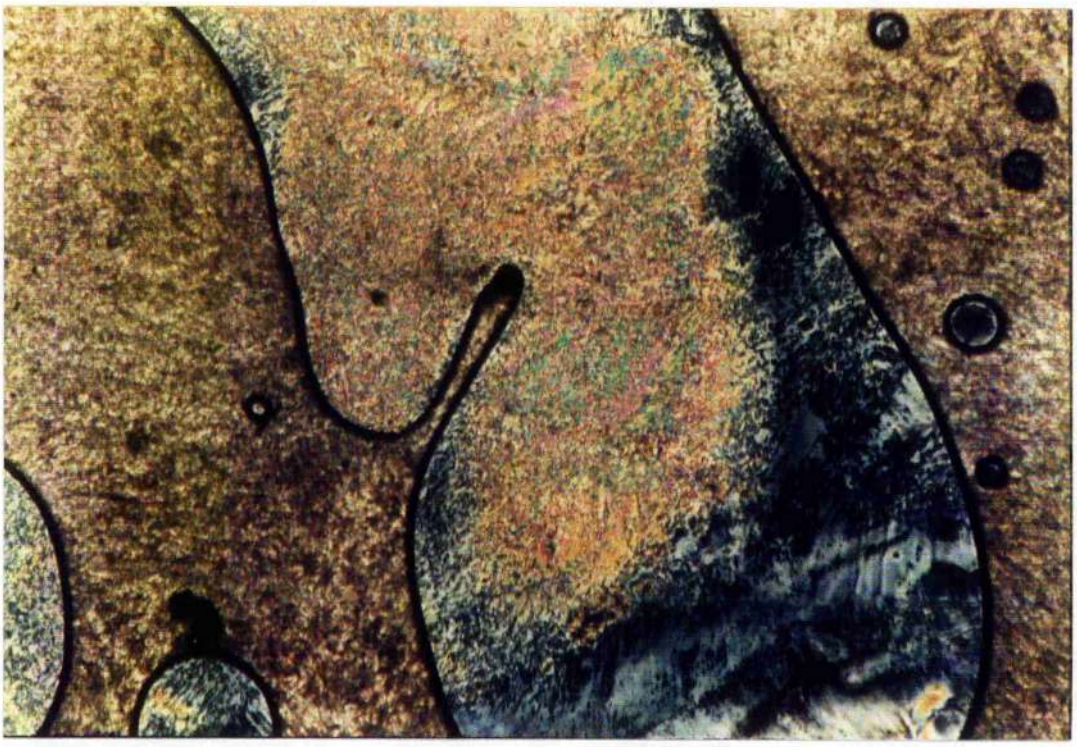


Plate 6 - the nematic phase of P13, contrasting the thick, grainy--textured areas and the thinner colourful and silver areas.

Plate 7 - the nematic phase of P13 after shearing.

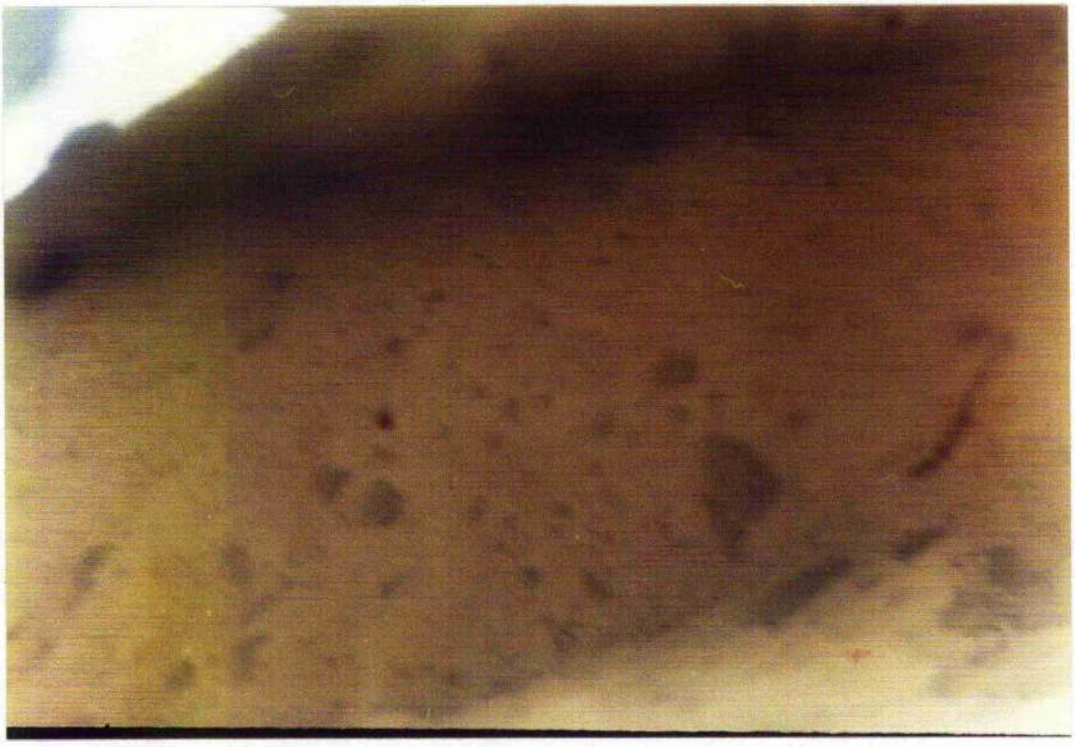


Plate 8 - the "rubber melt" obtaining by heating Po to 280 °C.

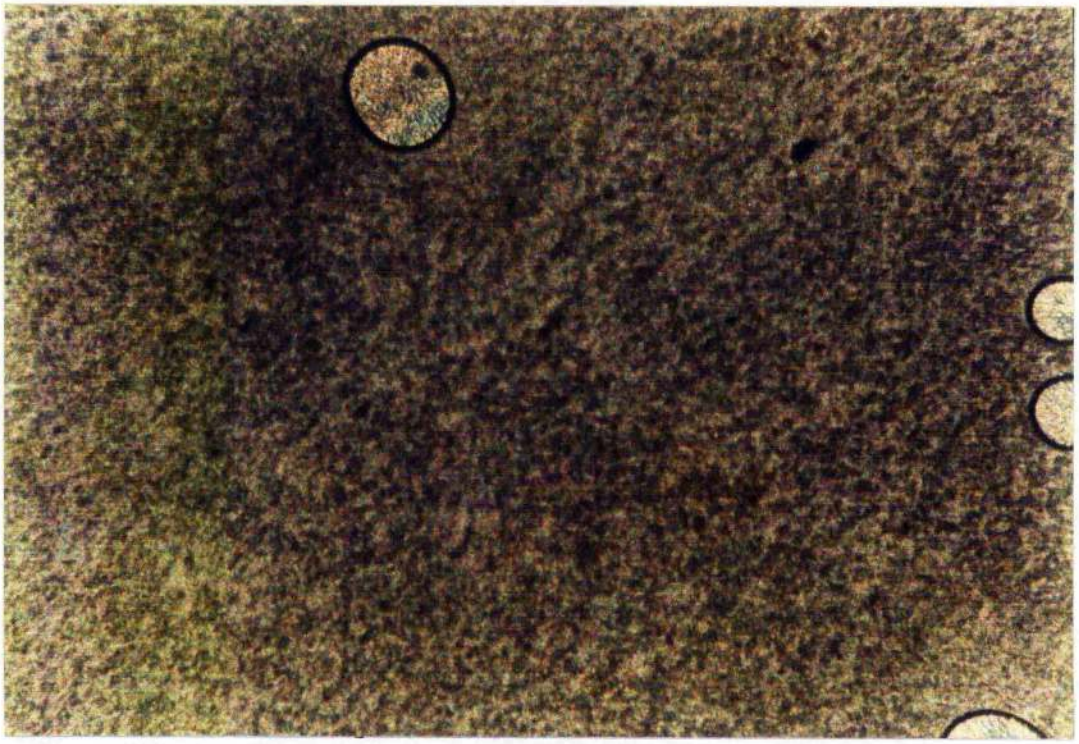


Plate 9 - the grainy-textured nematic phase of Po. The grainy areas are again thicker regions of the melt; the thinner regions are colourful, as in the "bubble".

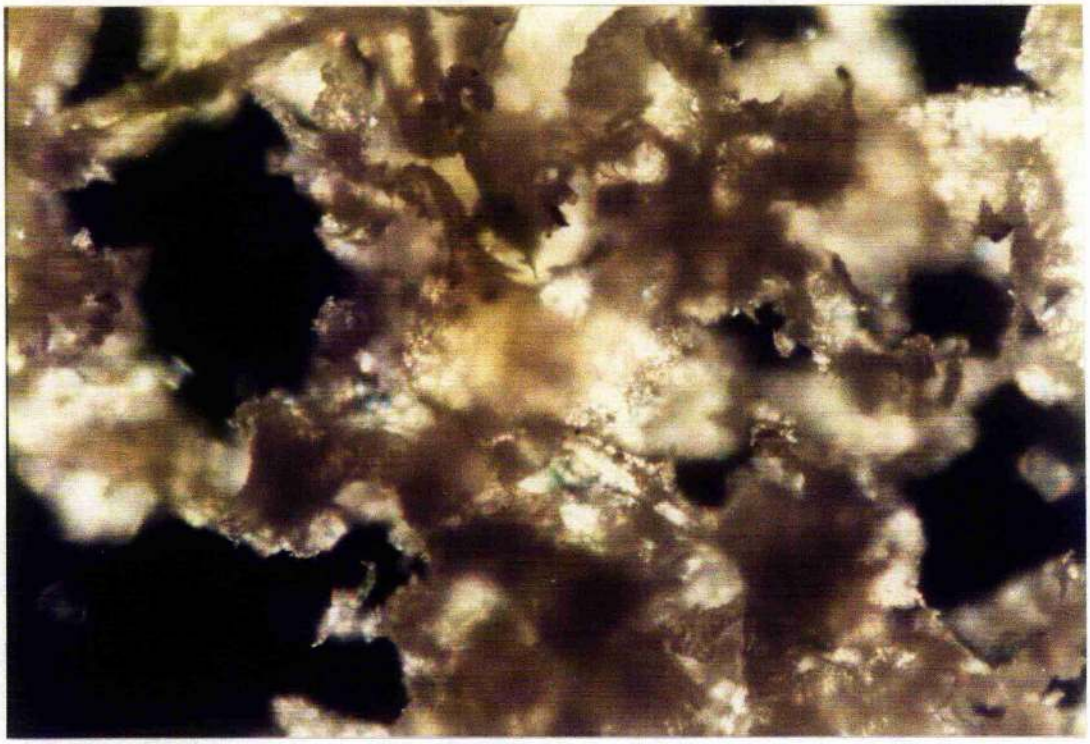


Plate 10 - small pieces of P15.

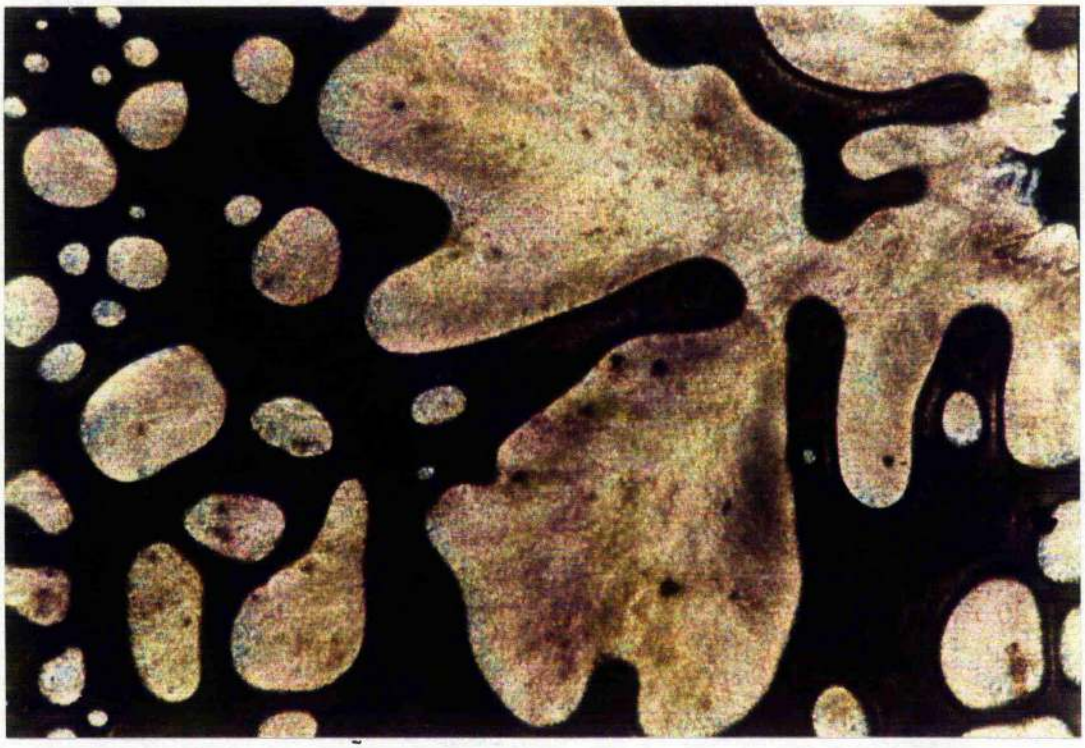


Plate 11 - P15 nematic phase. The thick areas are dark in colour; the thinner areas are "grainy" in appearance with some colour.

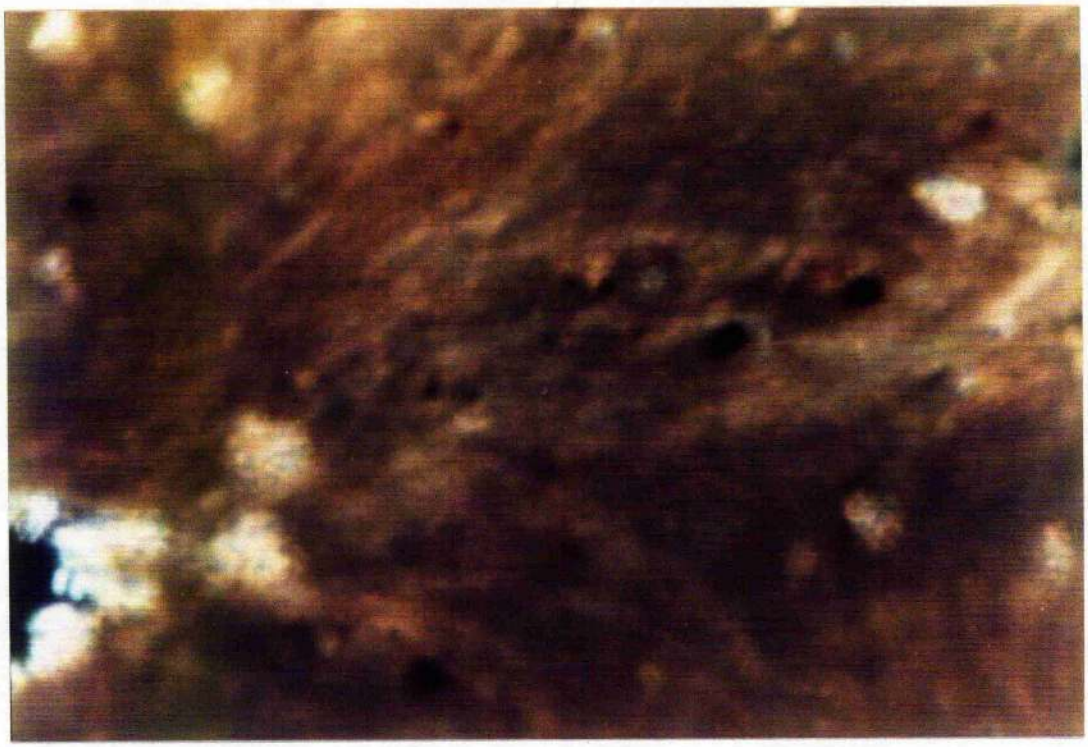


Plate 12 - P15 showing shear opalescence.

Plate 13 - P45 solid

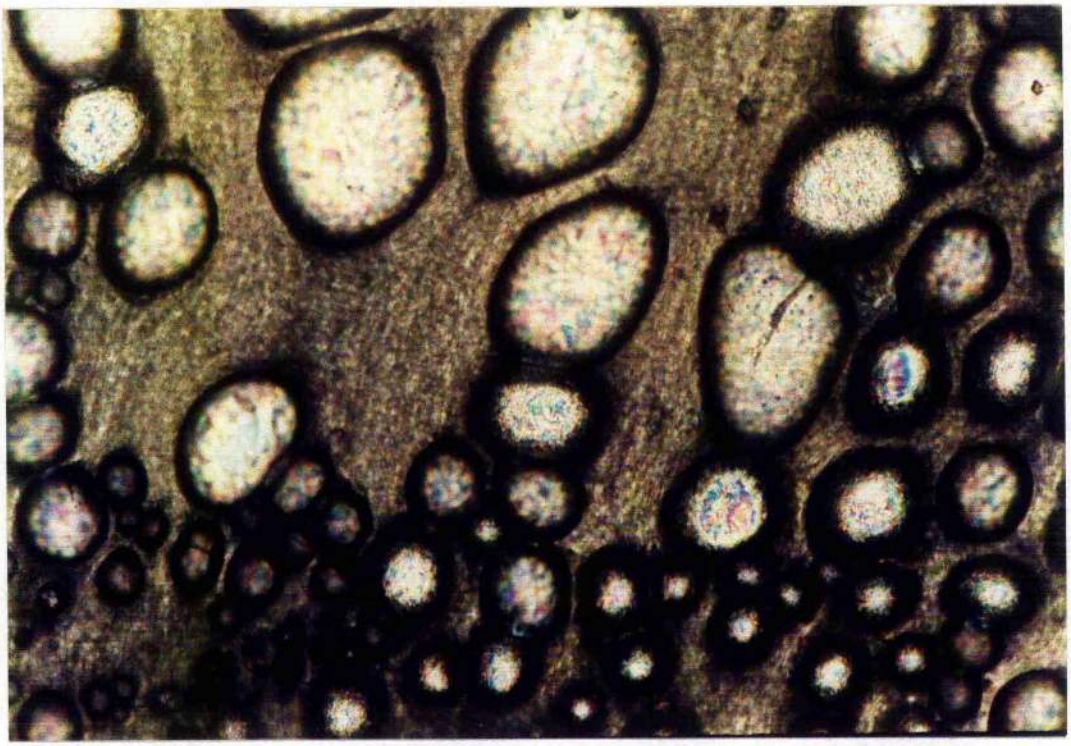


Plate 14 - P45 nematic phase. Thicker areas are once again grainy in appearance.

Plate 15 - P45 nematic phase showing threaded texture of the nematic

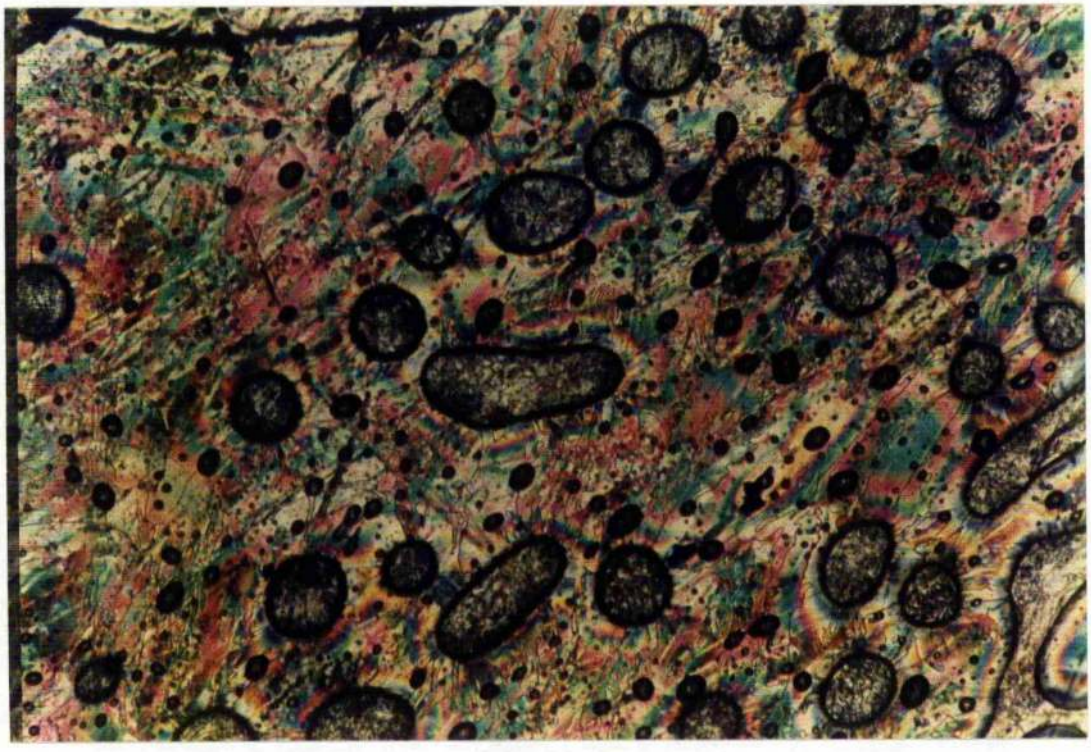


Plate 16 - P45 nematic phase at 350 °C - sample now thinner and showing more coloured effects.

3.3.4 Thermal Stability

The thermal stabilities of the 18 chosen polymers were assessed by thermogravimetric analysis (TGA) A Stanton Automatic Thermo-Recording Balance was used. The polymer samples were in the form of pressed discs (diameter 10 mm). The percentage weight loss was recorded as a function of temperature. The determinations were carried out in air.

The temperatures at which 2%, 5%, and 10% weight loss had occurred were recorded. The temperature at which 5% weight loss had occurred was taken to be the limit of thermal stability.

Table 6

P	2%	5%	10%
0	493	496	499
1	410	420	437
4	389	426	444
5	392	421	437
6	434	439	448
13	425	429	450
14	420	425	439
15	415	429	439
16	416	421	426
17	356	400	405
18	396	428	444
23	420	435	448
25	448	453	462
32	410	429	444
41	391	400	420
43	351	381	400
46	336	349	356
48	381	391	410

From Table 6 it can be seen that Po is the most thermally stable polymer. Regarding the series P1 to P32 and P48, P25 has a slightly higher value of Ts ($\sim$20 °C): this may be due to the fact that it is composed wholly of mesogenic units, as with Po; whereas P17 is slightly lower and is the only non-liquid-crystalline polymer. It should be remembered at this point that the monomeric 1,3,4-oxadiazole system degrades at temperatures slightly higher than 400 °C (Chapter 2, page 45), and this may account for the narrowness in the range of Ts for the majority of these polymers. In the case of P48, the slightly lower value of Ts may arise due to the rupture of the oxadiazole-oxadiazole bond, which has been proven to be relatively weak.[134]

The DSC thermograms can also be used to estimate the onset of decomposition, although this method is less accurate. Both sets of results were, however, found to be in good general agreement.

3.3.5 Solubility Studies

Aromatic copolyesters, due to their rigid rod structures are difficult to dissolve at low temperatures in concentrations of more than a few percent. Some solvents and solvent combinations that have been tried in this work are found in Table 7.

As most of these solvents are phenols or acids, care must be taken to prevent hydrolytic or exchange reactions from occurring, since this would obviously degrade the polymers and problems would thus arise in determining the molecular

Table 7

Solvent	Solvent Activity
p-Chlorophenol	Strong
p-Chlorophenol/tetrachloroethane	Strong
o-Dichlorobenzene/*p*-chlorophenol (50/50)	Strong
Phenol/1,1,2,2-tetrachloroethane/ *p*-chlorophenol (25/35/40)	Strong
Trifluoroacetic acid (TFA)	Weak
TFA/dichloromethane (60/40 or 30/70)	Strong
Phenol/1,1,2,2-tetrachloroethane (60/40)	Strong
Phenol/chloroform	Weak
Hexafluoroisopropanol	Weak
m-Cresol	Weak
o-Chlorophenol	Weak

weight of such polymers.

From the solvents in Table 7, it was found by trial and error that TFA/dichloromethane (30/70) was the best solvent, although by no means was it perfectly satisfactory.

Most of the other solvents in Table 7 were found to be unsatisfactory. Several solvents, such as HFIP and TFA, had no visible effect on most of the polymers. Other solvents, such as *p*-chlorophenol/tetrachloroethane and phenol/tetrachloroethane, caused the polymers to expand, but yet they would not dissolve.

The polymer solutions (concentrations ranging from 0.1 to 0.15 g/100 ml were prepared at room temperature in subdued light, by shaking the flasks containing the polymer and the solvent for up to 72 hours.

Although the combination TFA/CH_2Cl_2 (30/70) was the best solvent found, only 13 of the 18 polymers studied were totally soluble in this medium. The other 5 polymers were either unaffected, slightly dissolved or expanded. Details are given in Table 8.

Table 8

Po	Unaffected.
P1	Dissolved (12 h), green solution.
P4	Dissolved (24 h), green solution.
P5	Expanded and dissolved slowly (72 h), green solution.
P6	Unaffected.
P13	Dissolved (12 h), green solution.
P14	Dissolved (12 h), green solution.
P15	Dissolved (12 h), green solution
P16	Dissolved (12 h), clear solution
P17	Dissolved (12 h), clear solution
P18	Expanded and only slightly dissolved, yellow-green solution.
P23	Dissolved, light green solution
P25	Expanded and only slightly dissolved, olive-green solution.
P32	Dissolved (12 h), light green solution.
P41	Dissolved (24 h), dark green solution
P43	Dissolved (24 h), very dark green solution.
P46	Dissolved (24 h), almost black solution
P48	Dissolved only slightly, light green solution.

From Table 8, a very good correlation can be noted between solubility and composition of the polymers. Polymers with a large percentage of DPO are easily dissolved; the lower the concentration of DPO, the more insoluble the polymers become. This is especially noticeable with P1, P4,

P5 and P6. P1 and P4 dissolve readily (within 12 h), whereas P5 takes 72 h to dissolve and P6 is unaffected. P13 - P17 all contain a large proportion of DPO and are once again all soluble. P18 and P25, which have the DPO replaced by 27N and 15N respectively are virtually insoluble. However, in P23, half of the 27N is replaced by DPO and this polymer is now soluble. P32 contains DNO which is even more disruptive than DPO and thus the solubility of this polymer is expected. P41, P43 and P46 gave very dark solutions and it was feared that these polymers may be degrading in solution. However, when added to water, a polymer does precipitate and thus degradation, if occurring, is by no means total. It was expected that P48 would dissolve. However, it is assumed that the geometry of the two directly-connected oxadiazole rings is such that the chain-continuing bonds are parallel and oppositely directing (Chapter 2, page 50), and thus no angular disruption is present, allowing for closer packing of the polymer chains. The close packing of polymer chains reduces the quantity of solvent molecules that can penetrate the polymer, thus reducing solubility.

It was decided that the measurement of intrinsic viscosity for the polymers would give no great benefit, as the composition of every polymer is different and thus the results could not be interpreted as relating to the molecular weight of every polymer. Also, since the solvent used was corrosive, GPC could not be used to determine the molecular weight + the molecular weight distribution. Thus no such determinations have yet been performed.

3.4 COMPOSITIONAL SERIES

The remaining 32 polymers were less thoroughly investigated but the following trends were apparent in particular series.

27N Series

This series comprises the polymers P18 - P24. Replacement of the ANA in P18 by pABA to give P19, resulted again in an increase in the value of Tcn(1). When the ANA was replaced by mABA to produce P20, the resultant polymer was a black, brittle glass that was shown to be non-liquid-crystalline (Tci 245 °C). It was also observed that polymers containing the monomer ANA were more fibrous in appearance, compared to those containing pABA.

15N Series

The same general trends were noted in this series as in the 27N series. Replacement of ANA with pABA resulted in less fibrous polymers with higher values of Tcn(1). Replacement of ANA with mABA again gave a black, glassy, non-liquid-crystalline polymer (Tci 255 °C).

DPO/IA/ANA Series

In this series, the three polymers all have a 1:1 molar ratio of DPO and IA, but the number of molar equivalents of ANA is 1, 2 and 3 in P30, P15 and P31 respectively. P30 is a crumbly, non-liquid-crystalline polymer (Tci 370 °C). The two other polymers are, however, both brown, fibrous and very tough polymers which are liquid crystalline.

DNO Series

This series is comprised of the polymers P32 - P38. The general structure/Tcn(1) value trends, as noted in the 27N and 15N series, are once again evident. The ANA-containing polymers are more fibrous in nature with lower values of Tcn(1). P34, containing mABA, is a black glass (Tci 300 °C) as is the case with P20 and P27.

DPOA/DMOA/DPSA Series

P39 - P47 constitute the above series. All these polymers are smooth in texture, as opposed to fibrillar, and are easily broken. They all have much lower solid-to-nematic transition temperatures, and flow rapidly at these temperatures to produce threaded nematic melts. DSC thermograms are, in general, not very characteristic. However, general structure/Tcn trends appear. Those polymers formed from HQA have very noticeable Tcn peaks at higher temperatures than polymers derived from 15N, whose Tcn are either unobserved or very small, and which melt at lower temperatures.

Bis-oxadiazole Series

This series consists of the three polymers P48 - P50. P48 was a smooth but brittle, light brown polymer, whereas P49 and P50 were both rough textured, but still brittle. HSM revealed that P48 and P49 showed a liquid crystalline phase; P48 at 190 °C (this corresponds with an endotherm on the DSC thermogram), and P49 at 320 °C, (which also corresponds to an endotherm on the DSC thermogram at 310 °C). However, P50 was still solid at 350 °C by HSM observation;

but an endotherm is present on the DSC thermogram at 375 °C, and it may thus be liquid crystalline at this temperature, which was outside the range of HSM.

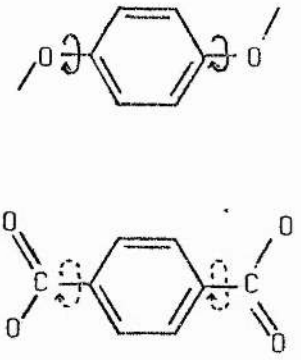
3.5 CONCLUSION

The most noticeable feature concerning the oxadiazole- (or thiadiazole-) containing polymers is the difference encountered between the diacetate and the dicarboxylic acid containing polymers. The oxadiazole-diacetate containing polymers are fibrous (especially those containing ANA) and some are remarkably tough, whereas the oxadiazole and thiadiazole-dicarboxylic acid containing polymers are smooth, may be glassy but are very easily fractured. The differences are not only visual, for there are differences observed in HSM and DSC - the most noticeable of which is the remarkably low solid-to-nematic phase transition temperatures of the dicarboxylic acid-containing polymers (P41, P43 and P46). As previously mentioned, these transitions are accompanied by a rapid flow into the nematic phase, very reminiscent of a normal crystal → melt type flow. It was thus suggested that the dicarboxylic acid-containing polymers were partly crystalline, although no x-ray data to date have been obtained to verify such a statement. The reason for the supposed partial crystallinity of the diacid-derived polymers and the amorphous character (or exceedingly low crystallinity) of the diacetate-derived polymers must lie in the structure of these units.

In an aromatic polyester, a diphenol unit has free rotation around the (aryl C)-O bond, (Figure 35), whereas

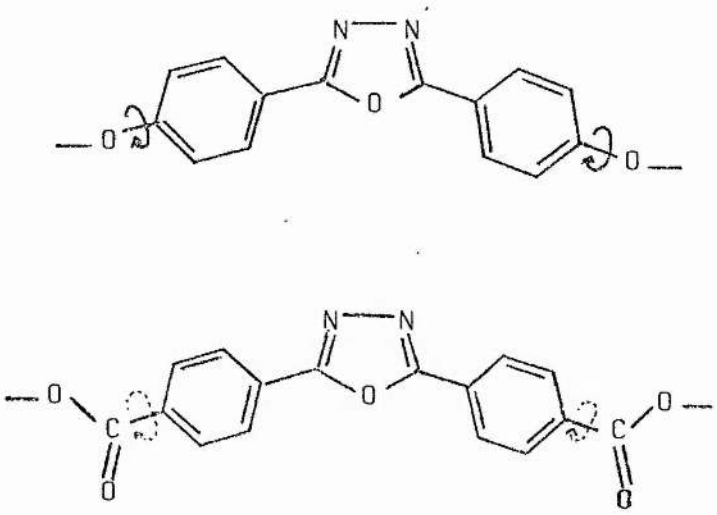
a dicarboxylic acid unit would be expected to have a reduced

Figure 35



rotation due to conjugation of the phenylene ring and the carbonyl group (Figure 3). In exactly the same way, such rotations may be envisaged to occur in the unit DPO, but to a lesser extent in DPOA (Figure 36).

Figure 36



It is thus believed that due to the reduced rotation in the DPOA structure, that this "freezing in place" may result in a more ordered structure, perhaps producing small areas

of paracrystallinity, or even crystallinity. On the other hand, using the same argument, the DPO unit is expected to result in an almost (if not totally) amorphous polymer since if it can rotate, and so cannot be "frozen" the degree of ordering that is expected to result is minimal.

With respect to Po, it appears that the 1,3,4-oxadiazole system, although thermally stable to temperatures of 400 °C produces polymers which are not as thermally stable as Po. These polymers are however stable enough to permit their fabrication into fibres (Chapter 4, page 128). Po is also more resistant to solvents than are those polymers based on an oxadiazole structure. However, the polymers based on the oxadiazole monomers, especially DPO, were very fibrous and slightly tougher than Po (although Po was itself by no means non-fibrous or weak).

It was thus decided to attempt the fabrication of several of these polymers into fibres to compare their tensile properties with those of conventional polymers.

CHAPTER 4

F I B R E S

4.1 MELT SPINNING

4.1.1 General Introduction

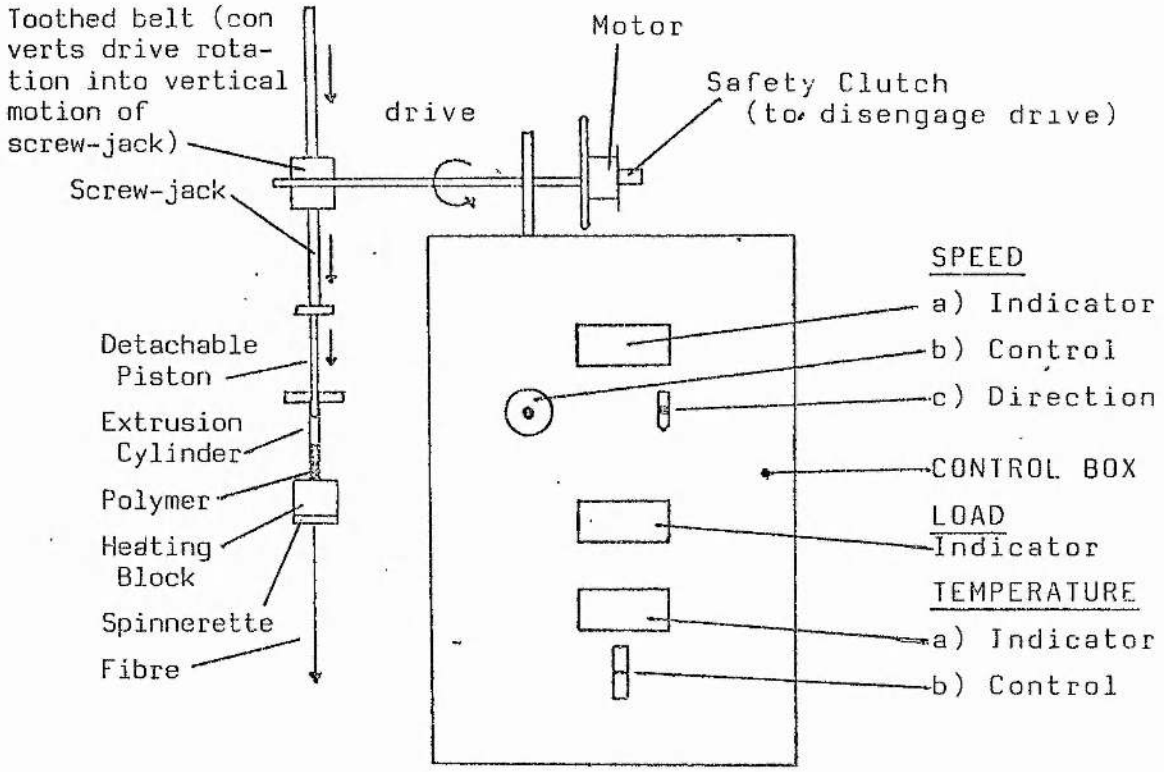
As the name "melt spinning" implies, a polymer melt is forced under pressure through a spinnerette to produce fibres which can be subsequently treated in a variety of ways. Of the 50 polymers prepared, the 18 which had already been characterised closely (*cf.* Chapter 3, page 89), were chosen for fabrication into fibres. As in the previous chapter, these 18 polymers are divided into several small groups for comparison purposes.

4.1.2 Description of The Apparatus

The equipment used was a small-scale Melt Spinning Unit, manufactured by Bradford University Research Ltd., and installed in the Scottish College of Textiles. The general features of the machine are shown, in simplified form, in Figure 37. The equipment is intended for the melt spinning of fibres under controlled and reproducible conditions from small samples of polymer, down to approximately 2 g in weight. All the components in contact with the polymer are constructed from stainless steel.

In order to spin, a polymer sample is placed within an extrusion cylinder which is bolted to the top surface of a heater block. The extrusion cylinders are produced with various diameters and capacities. A spinnerette is attached to the lower face of the heating block. The spinnerettes used were standard items available from Courtaulds Engineering Limited and can be obtained with single or multiple holes in

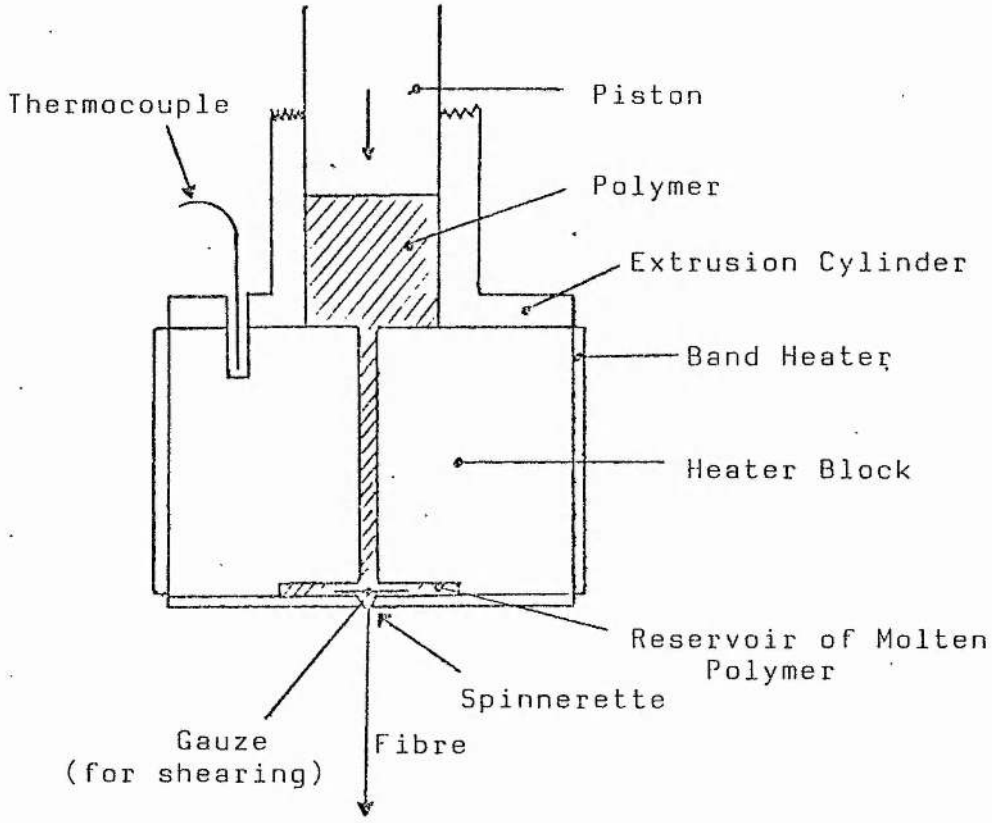
Figure 37



a wide range of sizes. In this work a single hole of diameter 0.75 mm was employed. The heating block is heated by means of a band heater clamped around it. This arrangement is shown in Figure 38, and discussed in more detail in Section 4.1.3.

The piston used to extrude the molten polymer is attached to the screw-jack by a stainless steel pin. The screw-jack is itself driven, *via* a toothed belt, by a motor which has a built-in safety clutch. The latter disengages the motor when an excessive load is encountered. When the load drops, the clutch connects the drive and in this way, damage to the apparatus is prevented.

Figure 38



Once filaments are being produced, they are collected on a take-up unit, which can collect filaments at speeds of up to 150 m/min. The unit consists of a pair of thread-advancing rollers and a take-up reel. At this stage in the proceedings it is a simple matter to vary such parameters as filament linear density and speed of extrusion or take-up to produce a range of samples for evaluation and determination of the optimum conditions of production.

4.1.3 Preliminary Spinning Experiments

These experiments were performed on a commercially available PET called "Melinex", which was obtained in the form

of small chips (4 mm^3). Two procedures are available for the melt spinning of such a polymer:

i) direct spinning, using the polymer pieces, or

ii) from a preformed "candle", made by fusion of the polymer pieces into one mass.

Preparation of Polymer Candle

The pre-forming cylinder of ½" diameter was used. A band heater was attached to the cylinder and the blanking plate securely bolted to the cylinder base.

The cylinder was then charged (up to 75% of its total capacity) with PET and positioned in the spinning apparatus. The heater was connected, and the thermocouple inserted. The temperature controller was set so as to soften the polymer without melting it (240 °C in the case of PET).

As the cylinder was heating, the piston was assembled and lowered until contact was made with the polymer. As the piston compresses the granules the load rises until the clutch releases. The motor is then left to run at a slow speed (*ca.* 0.2 mm/min) and after a period of time, as the temperature rises to the softening point of the polymer, the clutch re-engages and compresses the granules to about 2/3 of their original volume, forming a solid rod.

Once the polymer can no longer be compressed, the load rises once again and the clutch releases. The screw-drive is then disconnected and the heater switched off. When the temperature has fallen somewhat (say by 20 °C), the blanking plate on the base of the cylinder is removed and the drive

mechanism re-engaged, whereby the piston pushes the polymer candle out of the cylinder. As it emerges it is a solid rod with a smooth exterior, with the outlines of the granules still evident, and with no stickiness or evidence of melting.

Several PET candles were prepared by this procedure and stored for spinning at a later date.

Spinning

The ½" extrusion cylinder was bolted to the small heater block. To the lower face of the block a spinnerette was bolted, with a disc of fine stainless steel gauze inserted in the gasket (the gauze is not for filtration, but acts as a means of shearing the molten polymer so as to enable smoother flow through the spinnerette). A band heater was placed around the heating block and the assembly placed in position in the extrusion unit.

With the temperature controller set to a few degrees below the nominal melting point, (in the case of PET it was set at 255 °C, whereas Tci is 265 °C), a polymer candle, or loose granules of polymer, (if spinning is to be done directly), was placed in the cylinder; the piston was lowered on to the polymer. As the temperature approaches the set value, the load in the system is observed; when the polymer starts to melt the load should drop and extrusion of the polymer should commence. However, in this case at 255 °C no drop in the load was observed and thus the temperature was raised cautiously, in increments of 2 °C, until a drop in the load was observed. This occurred at 265 °C.

A droplet of the polymer collected on the lower face of the spinnerette. This was removed using a pair of tweezers, and the filament drawn out from this droplet was led around the already-rotating take-up rollers and then on to the take-up package.

It was found from several attempts to spin PET, both from candle and loose chips, that:

i) the flow of polymer is more constant when spinning is performed using a candle rather than loose chips;

ii) it was easier to collect the fibres at the lowest possible temperature, *i.e.* 265 °C. At this temperature the molten polymer was quite viscous and solidification of the fibres was rapid, whereas at higher temperatures, the polymer flowed so freely that collection of the filaments was exceedingly difficult;

iii) an extrusion rate of 2 mm/min gave filaments that were quite fine, but yet were easy to handle;

iv) a reasonably slow take-up rate of *ca.* 50 m/min was found to be adequate; higher rates produced too many breakages of the filament.

From the various spinning experiments performed, it was decided that an extrusion rate of 2 mm/min and a take-up rate of 50 m/min, at a temperature of 265 °C were the best conditions for the melt-spinning of PET using our apparatus.

These, apart from the temperature, were thus specified as standard conditions, at which to attempt the fabrication of the 18 other polymers.

4.1.4 Preparation of Polymer Candles

The candles of the 18 selected polymers were prepared by the method described above for PET. The temperatures at which the polymers were pressed, were taken at 30 - 50 °C below the temperature at which they were observed to form a "rubber melt" by HSM. Details are found in Table 9.

Table 9

Polymer	Temp. (°C)	Density (g/cm^3)	Spinning Temp. (°C)
PET	240	1.450	265
0	125	1.350	350
1	125	1.419	-
4	130	1.380	300
5	125	1.416	280
6	130	1.403	280
13	150	1.395	300
14	125	1.416	280
15	130	1.375	220
16	150	1.373	290
17*	150	1.389	290
18	130	1.379	275
23	140	1.381	210
25	125	1.391	220
32	125	1.392	210
41*	150	1.433	200
43*	120	1.377	200
46	100	1.398	160
48	125	1.460	175

All these polymers, with the exceptions of those marked *, sintered to give marble-like candles (the others had a gritty, crumbly appearance). P46 was very smooth and homogeneous in colour; it was believed that even at 100 °C this polymer was molten from HSM and DSC observations and this would explain the consistency of the candle produced.

Using a micrometer, the length of each candle was determined to ±0.1 mm. Since the diameter of the candle was known, the volume and hence the density could be calculated. (It must be noted that this measurement of density is only approximate since air-pockets may be present within some of the candles.) (Table 9)

It is seen from Table 9, that although Po has the lowest density, there is very little difference in value of all the rest, with the exception of P48, which is somewhat higher. There is thus no obvious correlation between these approximate densities and the composition of these polymers.

4.1.5 Melt Spinning of the Polymers

Using the same procedure as used for the fabrication of PET (page 124), the melt spinning of all 18 polymers was attempted. Details of the spinning temperatures are given in Table 9. For all spinning experiments an extrusion rate of 2 mm/min and a wind-on rate of 50 m/min were used.

Po spun very readily at 350 °C to yield off-white fibres which were easily handled and collected on the reel. P1 and P4, however, did not spin readily. P1, even at 390 °C (the maximum temperature attainable) appeared to be too viscous

to fabricate; there was also some degradation as indicated by discolouration and fuming. P4 also proved to be very viscous (although thermally stable), and it is believed that these two polymers were of too high molecular weight to be spun with ease. Only very small amounts of fibre (*ca.* 10 - 20 cm in length) were obtained from P4, and these were light brown in colour.

Of the next group (P5 - P32), P5, P6, P13, P15, P16, P18 and P23 were all spun readily and were collected on reels. The remaining polymers in this group, although spun, were found difficult to collect on reels due to breakages. These fibres were thus simply stored in polyethylene bags, away from direct light.

The remaining four polymers, P41, P43, P46 and P48, all produced fibres which were extremely brittle and broke very easily if any force was applied perpendicular to the fibre axis. They can best be described as resembling uncooked spaghetti.

4.2 FIBRE CHARACTERISATION

4.2.1 General

One of the main objectives of this work is the study of the structure-property relationships of Po with those polymers containing oxadiazole-based disruptors, especially DPO. In this section of the work, such an outlook was still used; characterisation techniques used were DSC, X-ray diffraction and tensile properties.

Of the techniques used, DSC was found to be the least

useful in revealing information about the fibres. Most thermograms consisted only of a sloping baseline, with degradation occurring at ~400 °C. The other two techniques are now considered in turn.

4.2.2 X-ray Diffraction

The five polymer fibres which appeared by visual inspection to be potentially the most useful (Po, P5, P6, P18, and P23) were examined by X-ray diffraction. Plates 17 to 21 show the patterns obtained photographically from the X-ray diffraction (XRD) originals. (The "full rings" that are apparent arise from the silver foil used for calibration and should thus be ignored.) The XRD patterns (Plates 17-21) indicate that all the samples are paracrystalline only, and that Po alone shows indications of the initial development of crystallinity.

All samples are, however, quite well oriented, the degree of ordering decreasing along the series Po, P6, P5, P18 and P23.

Meridional patterns indicate the presence of aperiodic reflexions typical for ANA-containing copolyesters. These patterns are most distinct in Po. These aperiodic meridional reflexions were analysed in detail by Blackwell *et al.*[135]

Thus the XRD patterns are of the type one would expect for fibres spun from a nematic mesophase, that were not treated further, *i.e.* annealed.

Table 10 gives details of Plates 17 - 21.

Table 10

Plate	Polymer	AA-monomer Composition*	
17	Po	$(HQA)_1$	
18	P6	$(HQA)_{\frac{3}{4}}$	$(DPO)_{\frac{1}{4}}$
19	P5	$(HQA)_{\frac{1}{2}}$	$(DPO)_{\frac{1}{2}}$
20	P18	$(27N)_1$	
21	P23	$(27N)_{\frac{1}{2}}$	$(DPO)_{\frac{1}{2}}$

*Plus $(TA)_1$ $(ANA)_2$

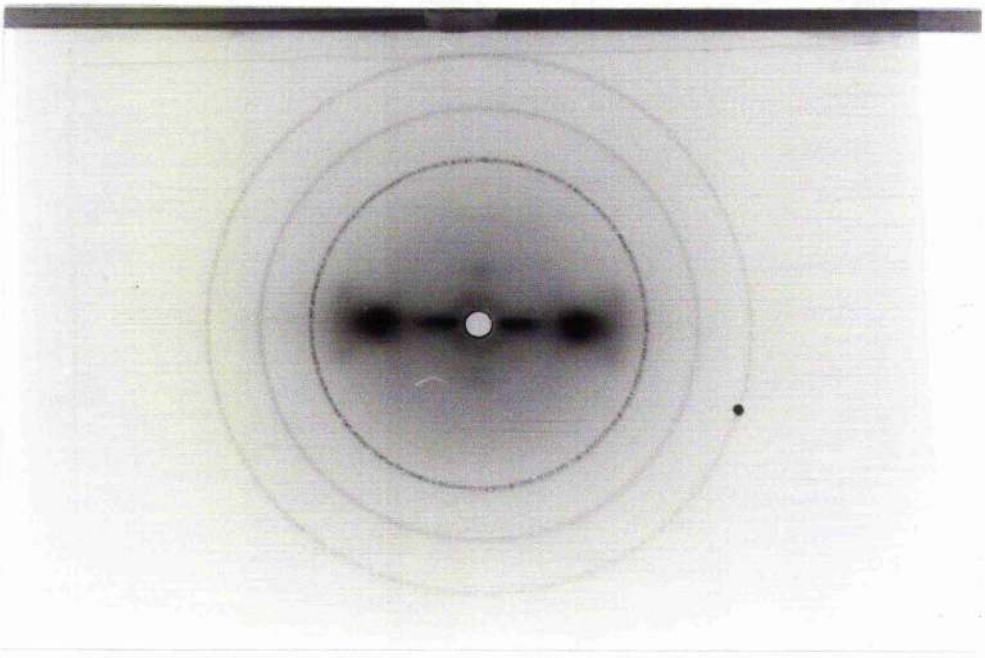


Plate 17

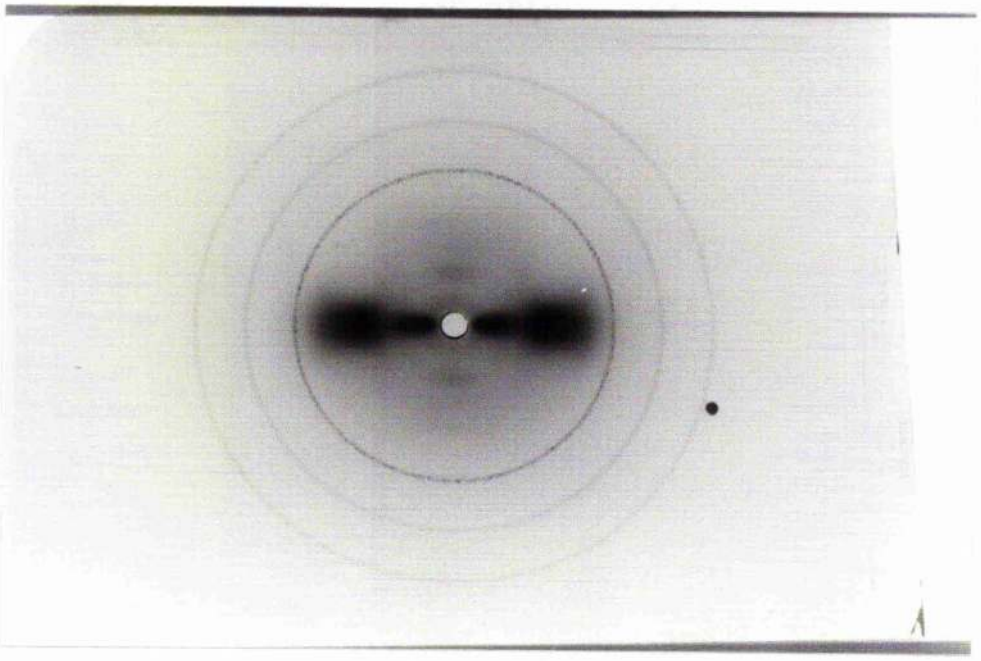


Plate 18

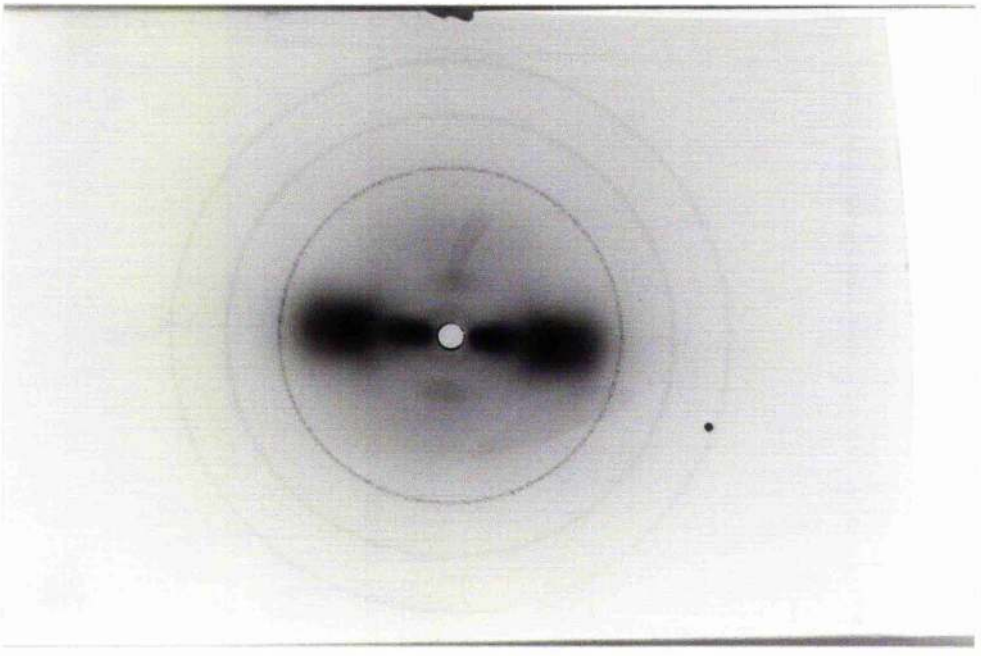


Plate 19

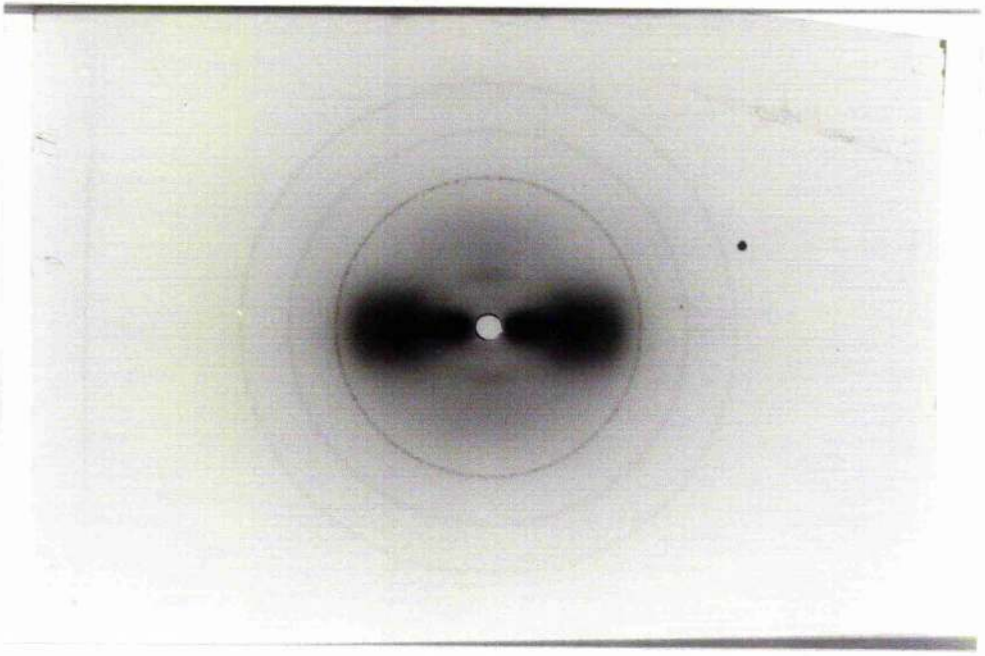


Plate 20

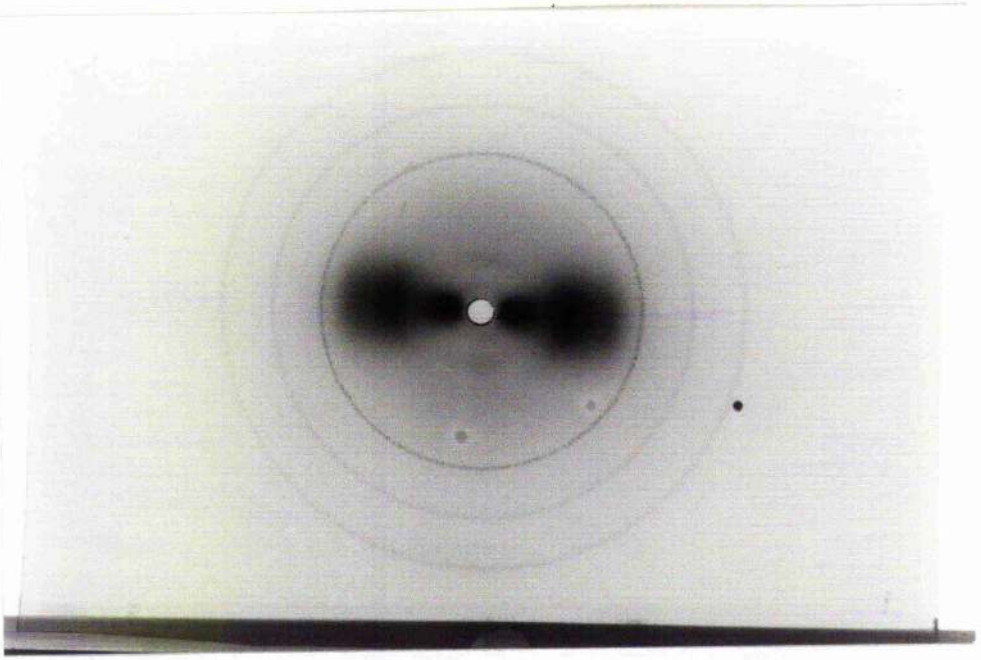


Plate 21

It is thus apparent that a gradual replacement of the HQA (in Po) by DPO to give P6, then P5, brings about a disruption in the polymer chain that can be seen from the XRD patterns as a "blurring" effect, due to the increasing randomness in the packing (although there is still quite a large degree of ordering present). Comparison of Plates 17 and 20 shows that total replacement of the HQA in P6 with 27N (which is comparable with DPO as a disruptor) creates a further increase in the disruption, leading to an even more diffuse XRD pattern. Replacement of half of the 27N with DPO (*i.e.* P23, Plate 21) creates even more disruption yet. This is due most probably to the randomisation created within the polymer due to the presence of two angular disruptors of differing lengths (although the angles of disruption are similar) (Chapter 3, page 98).

4.2.3 Tensile Strengths

The load-extension curves of single filaments were obtained by an Instron tensile tester. The linear density, tensile strength, initial modulus and the percentage extension at breaking point were calculated for every filament. The results are an average of 12 - 20 breaks.

The filaments were conditioned for at least 3 h in a standard atmosphere prior to testing. The resultant load--extension curves were expected to be Hookean as a result of the filaments being HSHM materials. However, although the curves were Hookean, they also possessed a toe which deflated the initial modulus values, although the value of

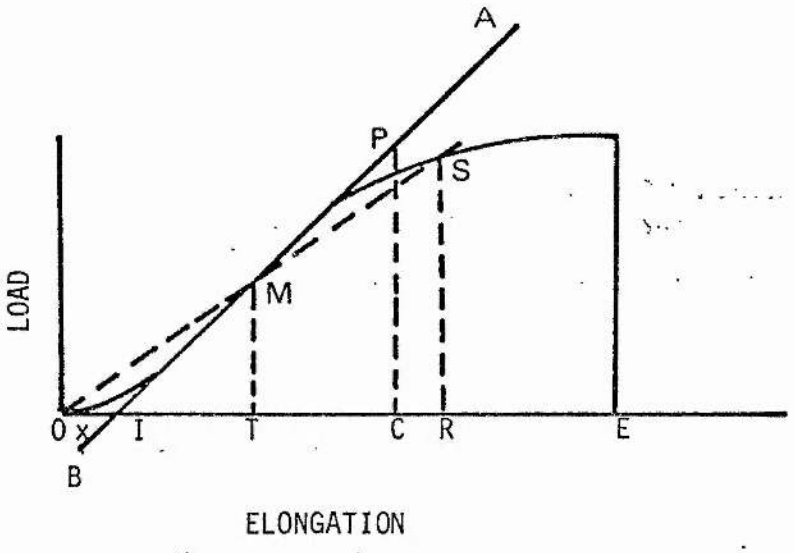
the load at breaking point was recorded correctly.

The problem was due to slippage of the filament in the jaws of the tensile tester and could not be prevented. However, its effect is reduced by using a longer length of the filament. This however results in a decrease in the tensile strength values due to the phenomenon known as the weak-link effect.[136] At these increased lengths however the toe may be disregarded, and thus more realistic moduli are obtained.

The length of filament used in these tests was 500 mm. The extension rate used was 5 mm/min.

Figure 37 illustrates a Load-Elongation Curve, where the line AB represents that used to determine the Initial Modulus

Figure 37



The definitions of the quantities calculated are:

i) linear density - mass per unit length. In this work all linear densities are expressed in decitex (1 dtex = 1 g per 10 Km of fibre).

ii) tensile strength - is the quotient obtained by dividing the breaking load (g) by the linear density.

iii) initial modulus - the slope of the initial straight portion of a stress-strain curve (Figure 37). The modulus is the ratio of the change in stress, expressed in grams-force per dtex, to the change in strain, expressed as a fraction of the original length.

iv) percentage elongation at the breaking load - the increase in length (of the original filament expressed as a percentage) at the breaking point.

The results of the tensile testing are shown in Table 11.

Table 11

Polymer	Linear density (dtex)	% Ext	Tensile Strength (gf/dtex)	Initial Modulus
PET	17.0	6.0	0.4	65
0	13.2	0.2	5.5	2,200
5	13.5	0.4	2.5	1,650
6	38.9	0.5	3.4	925
13	55.6	2.6	0.7	25
15	90.0	0.2	1.1	480
16	54.4	0.8	0.2	55
18	89.4	0.4	2.5	325
23	144.0	0.5	1.0	250

Table 12 shows the values of the percentage extension at breaking point, the tensile strength and the initial modulus

of all the polymers relative to the value of those of PET.

Table 12

Polymer	rel. % Ext.	rel. T.S.	rel. I.M.
PET	1	1	1
0	0.03	13.75	34
5	0.06	6.25	25
6	0.08	8.50	14
13	0.43	1.78	0.3
15	0.03	2.75	7
16	0.14	0.50	0.8
18	0.06	6.33	5
23	0.08	2.50	4

From the data in Table 12 it can be seen that the majority of the fibres have the tensile characteristics of a HSHM fibre, *i.e.* low extensibility, high tensile strength and initial modulus. The two noticeable exceptions are P13 and P16. Both these fibres show a considerable degree of inconsistency in their thickness, especially P16, which would explain the low values in tensile strengths that were obtained.

The inconsistency in the effective diameter of these fibres is believed to be a consequence of the spinning technique and not of the polymer structures. It is thus likely that if the basic spinning technique used were to be improved, then fibres having improved mechanical properties could be produced. Recommended improvements to the system would be a

means of regulating the flow of molten polymer, a means of directing and tensioning the fibre prior to being wound on to the reel, and a means of eliminating the abrasion that occurs as the fibre is wound on.

The overall conclusion from these results is that the standard polymer Po, which contains only mesogenic units, produces fibres with the best potential for some practical application. With the introduction of an angular disruptor (even in small amounts), although the temperature at which the polymer may be processed is lowered (which is an advantage), the thermal stability and tensile strength of such fibres are on the other hand reduced. The more angular disruptors are introduced, the more these effects are seen. It is also apparent that the nature of the angular disruptor is not important, *i.e.* the heterocyclic oxadiazole and thiadiazole systems and the carbocyclic 1,3-phenylene and 2,7--naphthylene systems all produce similar effects.

It must also be emphasised that since there was no measure of the relative molecular weight of the polymers, the results of the tensile testing and the initial fabrication of the fibres may be misleading, since with lower molecular weights, the tensile strength is lowered.

Since the spinning technique used was a standard, it is also possible that different fibres, even if of similar molecular weight, may have required different spinning conditions, such as extrusion rates and take-up rates, in order to have produced fibres with the optimum mechanical properties.

This work is only a preliminary survey, the refinement of which still remains to be achieved. Possible commercial exploitation of these polymers also lies in the future; several industrial concerns have expressed an interest in the work to date.

4.2.4 Photography

The following plates are all of P5 fibres.

Plate 22 - this shows the fibrillation that occurs when a fibre is broken.

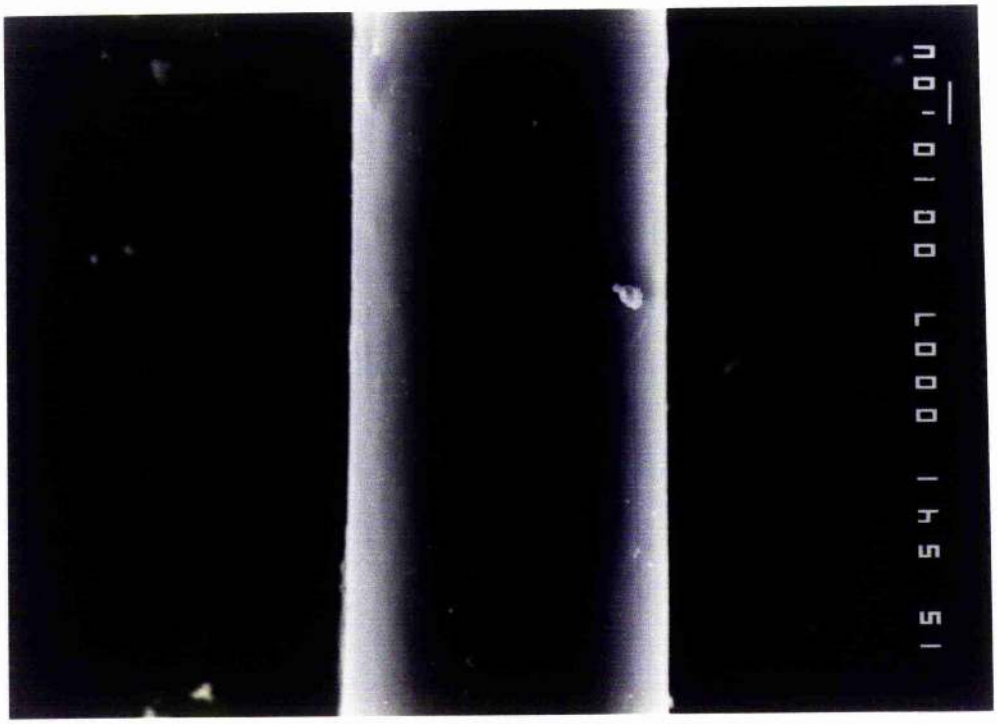


Plate 23 - this shows the nature of the "external" skin" of the fibre, which is smooth (very reminiscent of birch tree bark) with small deformation evenly spread over the surface.

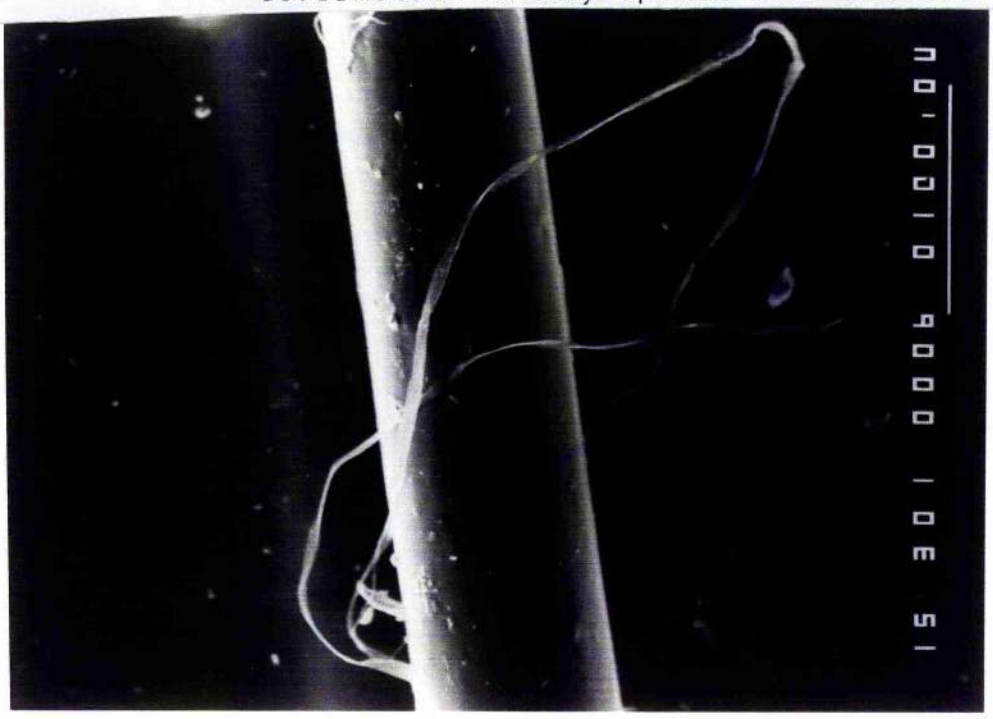


Plate 24 - this shows a paring occurring on the surface of the fibre.

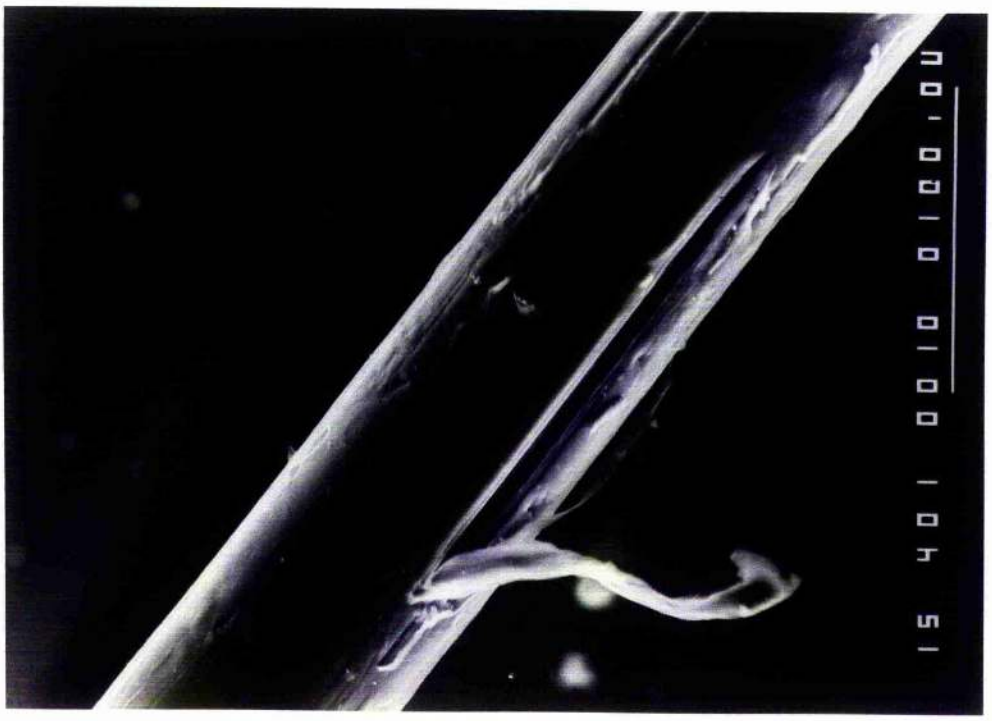


Plate 25 - this shows a large tear in the surface of the fibre. Note also the long thin tears at the bottom right of the fibre. These scorings were probably due to small metal particles or rugged edges scratching the fibre.

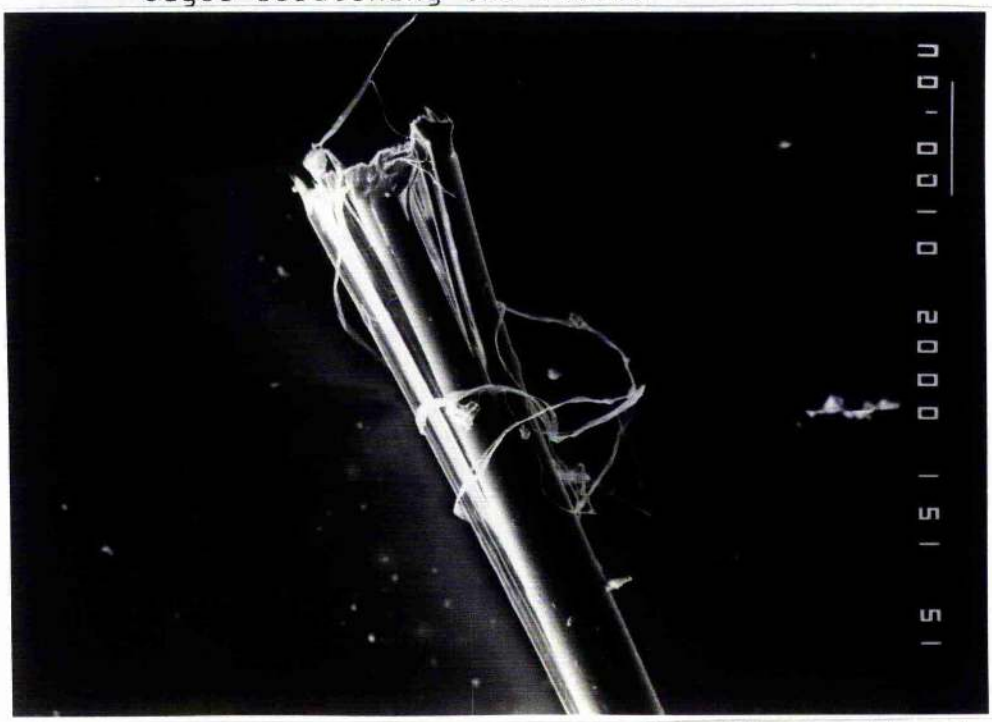


Plate 26 - shows the fibrillation in the fibre quite clearly and also shows the smooth skin that surrounds the fibre

On plates 23 - 26, the scale of the fibres (in µm) is indicated by the length of the white line (at the top right-hand side) and by the number directly to the left of the line. Thus in plate 23, the length of the white line is 10 µm, whereas in plate 24, it is 100 µm.

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Table 3

Polymer No.	Composition
0	$(HQA)_1\ (TA)_1\ (ANA)_2$
1	$(DPO)_1\ (TA)_1\ (ANA)_2$
2	$(DMO)_1\ (TA)_1\ (ANA)_2$
3	$(MPO)_1\ (TA)_1\ (ANA)_2$
4	$(DPO)_{\frac{3}{4}}\ (HQA)_{\frac{1}{4}}\ (TA)_1\ (ANA)_2$
5	$(DPO)_{\frac{1}{2}}\ (HQA)_{\frac{1}{2}}\ (TA)_1\ (ANA)_2$
6	$(DPO)_{\frac{1}{4}}\ (HQA)_{\frac{3}{4}}\ (TA)_1\ (ANA)_2$
7*	$(DPO)_1\ (TA)_1$
8	$(DPO)_1\ (DPOA)_1\ (ANA)_2$
9	$(DPO)_1\ (DPOA)_1\ (pABA)_2$
10	$(HQA)_1\ (DPOA)_{\frac{1}{2}}\ (TA)_{\frac{1}{2}}\ (ANA)_2$
11*	$(TA)_1\ (ANA)_2$
12	$(ANA\text{-}HQ)_1\ (TA)_1\ (ANA)_1$
13	$(DPO)_1\ (TA)_1\ (ANA)_1$
14	$(DPO)_1\ (TA)_1\ (ANA)_3$
15	$(DPO)_1\ (IA)_1\ (ANA)_2$
16	$(DPO)_1\ (TA)_1\ (pABA)_2$
17	$(DPO)_1\ (TA)_1\ (mABA)_2$
18	$(27N)_1\ (TA)_1\ (ANA)_2$
19	$(27N)_1\ (TA)_1\ (pABA)_2$

Table 3 (cont'd)

Polymer No.	Composition
20	$(27N)_1\ (TA)_1\ (mABA)_2$
21 †	$(27N)_1\ (IA)_1\ (ANA)_2$
22 †	$(27N)_1\ (IA)_1\ (pABA)_2$
23	$(DPO)_{\frac{1}{2}}\ (27N)_{\frac{1}{2}}\ (TA)_1\ (ANA)_2$
24	$(DPO)_{\frac{1}{2}}\ (27N)_{\frac{1}{2}}\ (IA)_1\ (ANA)_2$
25	$(15N)_1\ (TA)_1\ (ANA)_2$
26	$(15N)_1\ (TA)_1\ (pABA)_2$
27	$(15N)_1\ (TA)_1\ (mABA)_2$
28	$(15N)_1\ (IA)_1\ (ANA)_2$
29 †	$(15N)_1\ (IA)_1\ (pABA)_2$
30 †	$(DPO)_1\ (IA)_1\ (ANA)_1$
31	$(DPO)_1\ (IA)_1\ (ANA)_3$
32	$(DNO)_1\ (TA)_1\ (ANA)_2$
33	$(DNO)_1\ (TA)_1\ (pABA)_2$
34	$(DNO)_1\ (TA)_1\ (mABA)_2$
35 *	$(DNO)_1\ (IA)_1\ (ANA)_2$
36 *	$(DNO)_1\ (IA)_1\ (pABA)_2$
37 *	$(DNO)_1\ (TA)_1\ (ANA)_3$
38	$(DNO)_1\ (IA)_1\ (ANA)_3$
39	$(HQA)_1\ (DPOA)_{\frac{1}{2}}\ (IA)_{\frac{1}{2}}\ (ANA)_2$

Table 3 (cont'd)

Polymer No.	Composition
40	$(27N)_1\ (DPOA)_1\ (ANA)_2$
41	$(15N)_1\ (DPOA)_1\ (ANA)_2$
42 α	$(HQA)_1\ (DMOA)_1\ (ANA)_2$
43 β	$(15N)_1\ (DMOA)_1\ (ANA)_2$
44 γ	$(27N)_1\ (DMOA)_1\ (ANA)_2$
45 *	$(HQA)_1\ (DPSA)_1\ (ANA)_2$
46 γ	$(15N)_1\ (DPSA)_1\ (ANA)_2$
47	$(27N)_1\ (DPSA)_1\ (ANA)_2$
48	$(DP(OO))_1\ (TA)_1\ (ANA)_2$
49 †	$(DP(OPO))_1\ (TA)_1\ (ANA)_2$
50 *	$(DP(OMO))_1\ (TA)_1\ (ANA)_2$

All end temperatures, unless indicated otherwise below, were 320 °C.

* - No end temperature recorded as polymer solidified on the application of the vacuum.

† - Stirring of the polymer was only possible for a short period of time (20 mins), after the application of the vacuum, as the polymer gradually solidified.

α - End temperature of 300 °C

β - End temperature of 220 °C

γ - End temperature of 280 °C